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RP372

HIGHLY PURIFIED WOOD FIBERS AS PAPER-MAKING MATERIAL

By Royal H. Rasch,[1] Merle B. Shaw, and George W. Bicking

ABSTRACT

A semicommercial scale study has been made at the National Bureau of Standards of the manufacture of bond types of papers from commercial highly purified wood fibers for uses requiring permanency. As a part of the investigation, the experimental papers produced were tested for strength, chemical purity, and aging properties. The strength tests included bursting, tensile, and tearing strength and folding endurance. The chemical-purity tests included alpha cellulose content, copper number, acidity, and quantitative tests for the sizing materials present. The accelerated aging test used consisted of heating the papers in air to a temperature of 100° C. for 72 hours, and then measuring the extent of change in the various strength and chemical properties.

By studying the effects of variations in beating conditions on the properties of finished papers a method of beating well adapted for this kind of fiber was evolved. The papers had excellent strength properties, exceeding, in the case of the bond papers, the strength requirements of the highest-grade bond papers purchased by the Government Printing Office (U. S. A.) and, in the case of the currency-type papers, the strength requirements for United States currency. The experimental papers possessed also other characteristics desirable in these types of papers.

Some of the possible factors influencing the aging properties which arise in the process of converting pulp into paper were studied, including effects of beating; alum (acidity), rosin, and starch used in beater sizing; and glue, starch, alum, and formaldehyde used for surface sizing. The amount of beating required to produce the desired characteristics in the papers had no apparent effect upon the chemical properties of the fibers or upon their stability. A definite relation between the acidity of the rosin-sized papers and their stability was noted. A marked lowering in stability was caused by the use of excessive amounts of alum. By careful control of the acidity of the stock in the beater—i. e., amount of alum added to the beater—it was possible to prepare well-sized papers of very high stability. Other factors being alike, papers with the lowest rosin content had the best resistance to accelerated aging. In general the addition of starch in the beater caused an increase in the strength of the paper and had no deleterious effect upon the stability of the finished paper. The effects produced were practically the same for the two kinds of starch products used, one prepared by a process of acid hydrolysis and the other by a process of oxidation.

Unsized and rosin-sized papers were surface sized with glue and starch solutions. In general the bursting strength, tensile breaking strength, and elongation increased on surface sizing and the tearing strength decreased proportionally with the amount of size taken up by the basic paper. No such relation appeared to hold in the case of the folding endurance, which increased on surface sizing about 10 per cent on the average. In the case of the currency type papers, which had exceptionally high folding endurances before sizing, a slight decrease in folding endurance on surface sizing with glue was noted. For the specific samples of glue and starch used in this work, little difference in the final results obtained with them was noted. In general the stability of the papers toward accelerated aging was improved by surface sizing. This protective effect was somewhat more pronounced in the case of glue sizing than in the case of starch sizing. When alum was used in moderate amounts as a preservative for the glue or starch in the surface-sizing baths, it caused no deleterious effect on the paper as far as could be determined by the tests applied.

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I. INTRODUCTION

1. PREVIOUS STUDY OF HIGHLY PURIFIED WOOD FIBERS

In 1928 the National Bureau of Standards began a program of research on the study of highly purified wood fibers for the purpose of determining their value as a raw material for the manufacture of high-grade papers. These are wood fibers which have been refined to a high state of cellulosic purity as measured by such tests as copper number and alpha cellulose content. The first part of this investigation, which has already been published,[1] dealt with a comparative study of high purified wood fibers and papers prepared from them, and other types of paper-making fibers and papers, mostly commercial. The results of this work indicated that wood fibers can be obtained with sufficient strength and purity for conversion into the higher grades of writing papers where durability and longevity are essential requirements.

[1] R. H. Rasch, A Study of Purified Wood Fibers as a Paper-Making Material, B. S. Jour. Research, vol. 3 (RP 107), pp. 469–506, September, 1929.

2. PURPOSE AND PLAN OF INVESTIGATION

The conclusions drawn in the publication referred to were necessarily somewhat limited, because of the fact that complete information was not available as to the history of the various papers and paper-making raw materials tested. In the ordinary course of commercial production it is difficult to obtain important data on the many variables in manufacture which may influence markedly the permanence of paper and its ability to withstand continual handling. Therefore it was considered desirable to supplement the tests of commercial papers with similar tests of papers made in the bureau paper mill under carefully controlled conditions, where complete data on the various steps in the manufacturing processes could be obtained. The plan of investigation adopted includes unit studies of all the important types of commercial chemical wood fibers and rag fibers commonly used in the manufacture of record papers by means of their conversion into papers under semicommercial mill conditions, and subsequent thorough testing of these papers. It was realized that some incidental study of the important variables involved, such as beating and sizing operations, and, in the case of rag half-stock preparation, cooking and bleaching, would be necessary in order to gain the information required to develop the optimum qualities in papers prepared from each of the fibrous raw materials under consideration.

Knowing the exact details of manufacture and the test results obtained on papers manufactured under those conditions, it was expected that definite information could be obtained on the various fibers with respect to (1) the highest quality of paper possible to make from each of them under favorable conditions, (2) how to obtain this quality, and (3) the manner and the extent to which the quality of the paper is affected by the raw materials and by the variations commonly encountered in processing them.

This paper deals with such study of a grade of commercial highly purified wood fibers prepared particularly for use in such papers as bonds and ledgers. Richter has recently reported on the results of a similar investigation of the durability of purified wood fibers.[3] Similar tests of other types of fibers are in progress.

II. PAPER-MAKING EQUIPMENT

The bureau paper mill contains complete equipment for the manufacture of practically all types of paper under conditions which simulate those of industrial mills. Complete descriptions as well as photographs of this equipment may be found in previous bureau publications.[4]

III. PAPER-MAKING PROCESSES

1. BEATING AND PAPER-MACHINE OPERATION

Details of the beating and paper-machine operations as carried out in the bureau paper mill are thoroughly described in previous publications.[5]

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[3] Durability of Purified Wood Fibers, Jour. Ind. Eng. Chem., 23, No. 4, pp. 371–380, April, 1931.

[4] M. B. Shaw and G. W. Bicking, Caroá Fiber as a Paper-Making Material, B. S. Tech. Paper No. 340; also M. B. Shaw, Equipment and Research Work of the Bureau of Standards Paper Mill, Paper Trade Jour., vol. 89, No. 19, pp. 60–63, Nov. 7, 1929.

[5] M. B. Shaw and G. W. Bicking, Research on the Production of Currency Paper in the Bureau of Standards Experimental Paper Mill, B. S. Tech. Paper No. 329, and Further Experimental Production of Currency Paper in the Bureau of Standards Paper Mill, B. S. Jour. Research, vol. 3 (RP 121), pp. 899–926, December, 1929.

2. BEATER SIZING

(*a*) ROSIN

Rosin is the material most widely used for sizing the fibers in the beater to impart water resistance to paper. The size is made by digesting rosin with soda ash (Na_2CO_3) or caustic soda (NaOH) to form the sodium salt, a solution of which is added to the stock in the beater. Rosin is precipitated onto the fibers by subsequent addition of paper-maker's alum, aluminum sulphate, $Al_2(SO_4)_3.18\ H_2O$. The rosin size used in the present work contained about 33 per cent free rosin, held emulsified in the solution of sodium resinate.

(*b*) STARCH

When starch is used in the beater it is practically always used in conjunction with rosin size, as it does not itself impart water-resistant properties to paper. Two general types of commercial beater starch were used in this work; one said to be prepared by a process of acid hydrolysis, the other by an oxidation process.

In preparing the starch paste and in adding it to the beater the aim was to approximate the current commercial practice as far as possible. In making the paste, 1 part of starch (air-dry) was allowed to soak for about one-half hour in about 5 parts of cold water, after which time the mixture was brought up to a temperature between 140° and 160° F. It was kept at this temperature until the starch had swelled to the proper extent, and then was cooled. When used together with rosin size, the starch paste was added to the beater one hour after the latter and one hour before the addition of alum.

3. SURFACE SIZING

Most high-grade bond and ledger papers are surface coated with a film of glue or starch to improve the writing quality, resistance to wear, and various other properties.

(*a*) GLUE

The glue sizing bath consisted of a 4 per cent solution of a high-grade hide glue. In order to observe the effect of alum on the properties of the papers, sizing treatments were made with and without the presence of alum. In one experiment the use of formaldehyde as a preservative was tried. The sizing baths were maintained at approximately 130° F. The paper to be sized was passed through the heated solution, then between a pair of squeeze rolls to remove excess size, and finally dried in a festoon drier at a temperature of 110° to 120° F. The desired finish was imparted to the paper by supercalendering.

(*b*) STARCH

The procedure for surface sizing with starch was essentially the same as that for sizing with glue. As in the case of beater sizing, two types of commercial starch were used, one prepared by a process of acid hydrolysis, the other by an oxidation process. In preparing the solution for sizing, 1 part of starch was allowed to soak for one-half hour in 4 parts of cold water, and then the mixture was heated to a temperature of 165° F. When the proper swelling had taken place, sufficient water was added to make a 4 per cent solution.

IV. TEST METHODS

1. METHODS OF THE TECHINAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY[6]

The official T. A. P. P. I. methods for determining weight, bursting strength, thickness, folding endurance, tensile breaking strength, tearing strength, opacity, ash, resin, starch, and glue were used. The methods for sizing quality [7] and wet rub [8] were those developed at the bureau.

2. CHEMICAL TESTING METHODS

(a) TITRATABLE ACIDITY

Determinations of the titratable acidity were made on extracts of ground paper (Kohler-Hall method) [9] and directly on suspensions of the ground paper. Both procedures were outlined in a previous publication.[10]

(b) pH OF PAPER EXTRACT

The pH of the papers was determined colorimetrically on extracts of the ground samples with the Acree-Fawcett isohydric indicators.[11] It has been found that many of the extracts of paper are so weakly buffered or so dilute that their pH value is noticeably altered by the addition of the overneutralized commercial indicator solutions. In order to avoid this source of error, the isohydric indicator method was employed. These indicators are adjusted at intervals of 0.2 pH throughout their effective range. By preliminary trials the approximate pH of the unknown is located; then the final determination is made with an indicator of that pH.

The procedure used for preparing extracts of the paper for pH measurement was as follows: Into a suitable Pyrex flask containing 2.5 g of the air-dry ground paper sample was added 125 ml of boiling distilled water. The flask was fitted with an air condenser and placed in a steam bath. During the period of digestion the flask was shaken occasionally to keep the fibers distributed. At the end of one hour the suspension was poured onto a Büchner funnel. The filtrate was returned through the fiber pad formed on the funnel in order to remove any fibers. This clear filtrate was poured immediately into a 125 ml Erlenmeyer flask which was tightly stoppered. The test for pH was made as soon as the extract attained room temperature.

(c) ALPHA CELLULOSE CONTENT AND COPPER NUMBER

The alpha cellulose content and copper number procedures used were described in detail in a recent publication, which reports the results of a study made to develop improved procedures.[12]

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[6] Copies of the paper-testing methods of the Technical Association of the Pulp and Paper Industry may be obtained from the secretary, at 370 Lexington Avenue, New York, N. Y.

[7] F. T. Carson, Measurement of the Degree of Sizing of Paper, B. S. Tech. Paper No. 326.

[8] F. T. Carson and F. V. Worthington, A Wet Rub Tester for Paper, Paper Trade Jour., vol. 84, No. 2, pp. 45-46, Jan. 13, 1927.

[9] Kohler-Hall, Acidity in Paper, Paper Industry, vol. 7, No. 7, pp. 1-5, October, 1925.

[10] R. H. Rasch, Accelerated Aging Test for Paper, B. S. Jour. Research, vol. 7 (RP 352), pp. 465-475, September, 1931.

[11] S. F. Acree and Edna H. Fawcett, The Problem of Dilution in Colorimetric H-Ion Measurements—I. Isohydric Indicator Methods for Accurate Determination of pH in Very Dilute Solutions, and II. Use of Isohydric Indicators and Superpure Water for Accurate Measurement of Hydrogen-Ion Concentrations and Salt Errors. Parts I and II published, respectively, in Jour. Bacteriology, 17, No. 3, pp. 163-204; March, 1929, and Jour. Ind. Eng. Chem. (analytical edition), vol. 2, No. 1, pp. 78-85, Jan. 15, 1930.

[12] J. O. Burton and R. H. Rasch, The Determination of the Alpha Cellulose Content and Copper Number of Paper, B. S. Jour. Research, vol. 6 (RP 295), pp. 603-619, April, 1931.

3. ACCELERATED AGING TEST

The accelerated aging test or stability test employed in the present study consists of exposing the paper specimen under examination to a current of air at 100° C. for 72 hours and then observing to what extent the paper is altered in its several properties. The assumption made is that the changes produced in the paper parallel those produced under more normal conditions sufficiently to permit estimates of the probable relative longevity of papers. In a recent publication it was shown that this test arranged a series of Government writing papers of various grades in the expected order of permanence.[13]

In the present study physical and chemical tests previously outlined and described were made on the original papers. For the purpose of studying the aging qualities of the various papers the bursting strength, tensile breaking strength, per cent elongation at rupture, folding endurance, tearing strength, alpha cellulose content, and copper number were determined on the papers both before and after they had been subjected to the heat treatment. It is well known that paper may vary considerably in strength at different areas; therefore care was taken that the sample used for the heat test should be as nearly representative of the control sample as possible. In this work 10 sheets (10½ by 16 inches), so selected as to be representative of the whole machine run or tub sizing run, as the case happened to be, were divided into two sets, 10½ by 8 inches. One half was used for the control tests, the other half was subjected to heat treatment and subsequent testing. The portions of paper left over from the strength tests were ground for the chemical tests. This method of sampling seemed to be adequate for all the strength tests with the exception of the folding endurance. In the latter case further precautions were taken designed to minimize the possibility of large errors. The details of this procedure will be the subject of a subsequent report. Duplicate aging tests of 13 different papers using this procedure showed that the maximum variation of the retention value (ratio of folding endurance of heated paper to folding endurance of original paper) from the average was 10 per cent, and that the average variation for all papers was 4 per cent.

V. TESTS OF PAPER-MAKING FIBER USED

All the experimental papers prepared in the bureau paper mill for this work were made from the same lot of highly purified wood fibers representative of a commercial product. A representative sample of this pulp was tested, with results as given in Table 1.

TABLE 1.—*Tests of paper-making fiber used*

	Original sample	Sample heated at 100° C. for 72 hours
	Per cent	*Per cent*
Alpha cellulose content	• 91.9	91.6
Beta cellulose content	2.9	
Gamma cellulose content	5.2	
Copper number	.64	.77
Pentosans	3.50	
Resin	.27	
Ash	.17	

• The same determination made on ¼-inch square of the pulp sheet gave a result of 93.7 per cent. Many methods for the determination of alpha cellulose content, including the tentative standard method of the American Chemical Society, specify that the sample shall be in the form of squares.

[13] See footnote 10, p. 769.

VI. MANUFACTURING DETAILS AND TEST DATA FOR PAPERS

1. UNSIZED PAPERS

(a) HAND SHEETS

(1) EFFECT OF BEATING ON DEVELOPMENT OF STRENGTH PROPERTIES.—The character and many properties of paper, particularly strength, are determined in large part by the beating technic employed. The duration of beating and the manner of lowering the beater roll are both factors of importance in producing the desired strength characteristics in the paper. The treatment given the fibers in the beater differs considerably for different fiber materials and according to the type of paper being made. Some fibers "hydrate" very rapidly

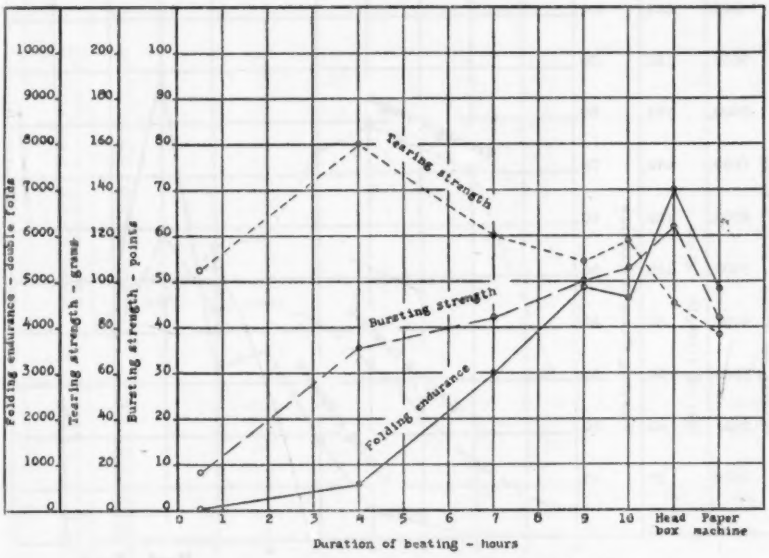

FIGURE 1.—*Strength properties of hand sheets*

Head box-Jordan and screened stock. Paper machine-test results on paper-machine products.

others exceedingly slowly. This study was confined to the development of types of high-grade writing papers, and therefore it was necessary to determine the beating procedure best designed to impart the high strength and other desirable characteristics important to this kind of paper.

The progressive development of strength with beating may frequently be satisfactorily and more conveniently studied by converting the fibers into hand test sheets, instead of by the slower and more expensive process of converting them into paper on a paper machine. In the present study hand sheets of stock taken at different intervals throughout the course of a beating were made. The strength values obtained on two runs are presented in Figures 1 and 2, which are typical of those obtained on several such runs. Standardized equipment and procedures have been developed at the bureau for the preparation of fiber hand sheets. For a detailed description of the pro-

cedure the reader is referred to an earlier publication containing that information.[14]

Figure 1 shows the maximum folding endurance was reached in approximately 9 to 10 hours of beating. The development of bursting strength followed along roughly with that of folding endurance. The tearing strength, however, reached its maximum in 3 to 4 hours and then decreased with further beating. While the folding endurance is considered the best indication of a paper's resistance to wear, it is essential that this factor be not developed to the disadvantage of the other desirable properties. In this case it was decided that a better balance between the folding endurance and the tearing strength would be had if the duration of beating were somewhat short of that

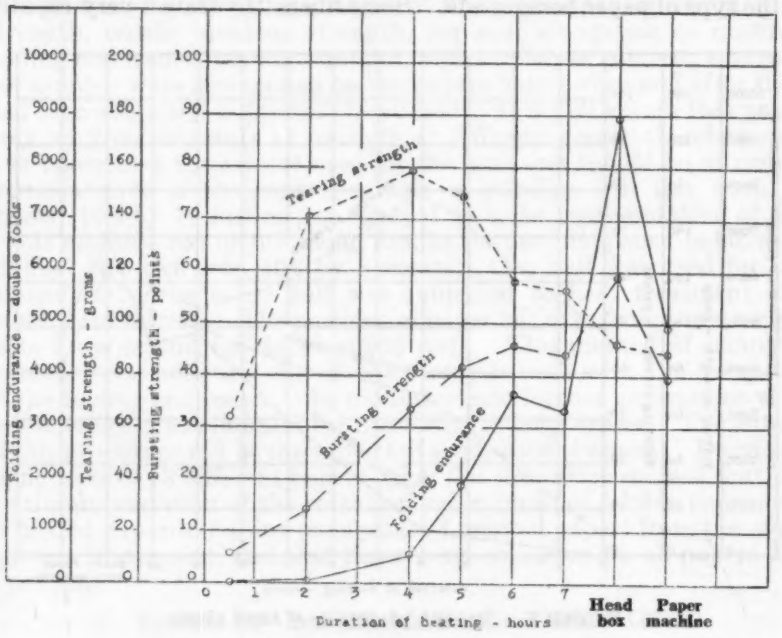

FIGURE 2.—*Strength properties of hand sheets*

Head box-Jordaned and screened stock. Paper machine-test results on paper-machine products.

required to give the maximum folding endurance and bursting strength. With excessive beating it would seem that an increased formation of cellulose gel takes place. While this material, by virtue of its cementing properties, increases the folding endurance and bursting strength, it decreases the tearing strength and the opacity, and, further, may have an undesirable hardening effect upon the paper. The most desirable kind of beating for bond papers is probably one which is sufficiently prolonged to develop the maximum felting properties, through brushing out and fraying of the fibers, but not so prolonged or drastic as to result in much cutting of the fibers or in the development of excessive amounts of cellulose gel.

[14] M. B. Shaw, G. W. Bicking, and L. W. Snyder, The Preparation of Fiber Test Sheets, B. S. Jour. Research, vol. 5 (RP190), pp. 105–114, July, 1930.

TABLE 3.—*Data on unsized and beater-sized papers*

UNSIZED PAPERS

Paper machine run No.	Beating interval	Freeness of stock		Rosin size, amount rosin based on dry fiber	Alum, amount based on dry fiber	Starch size, amount based on dry fiber	Acidity of stock at head box	Physical tests																			
								Aging test		Weight, 500 sheets, 25 by 40 inches	Bursting strength	Ratio of bursting strength to weight	Thickness	Folding endurance			Folding endurance in per cent of initial			Tensile breaking strength			Elongation at rupture			Tearing	
		After beating	At head box					Temperature	Duration					Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	
	Hours			*Per cent*	*Per cent*	*Per cent*	*pH*	*° C.*	*Hours*	*Pounds*	*Points* [2]	*Per cent*	*Inch*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	*kg*	*kg*	*kg*	*Per cent*	*Per cent*	*Per cent*	*g*	
759	[1] 10	110	56	0	0	0				51.9	42.0	81	0.0035	4,170	5,490	4,830				10.2	5.5	7.9	3.5	10.4	7.0	81.6	
								100	72	51.4	42.1	82		3,780	5,460	4,620	91	99	95	10.0	5.5	7.8	3.3	9.8	6.6	84.4	
760	[1] 12	81	36	0	0	0				57.2	41.6	73	.0035	5,250	3,910	4,580				9.5	5.4	7.5	3.0	10.6	6.8	94.4	
								100	72	56.2	41.2	73		5,260	3,770	4,520	100	96	98	10.1	5.4	7.8	3.4	10.3	6.9	97.2	
760	12	81	62	0	0	0				55.1	37.9	69	.0036	4,310	2,970	3,640				9.2	5.2	7.2	2.9	9.3	6.1	89.6	
								100	72	55.0	37.5	68		4,130	3,000	3,570	96	101	99	9.7	5.2	7.5	3.2	9.0	6.1	92.4	
761	7	147	128	0	0	0				54.0	37.1	69	.0036	3,780	2,160	2,970				9.2	4.6	6.9	3.1	8.6	5.9	106.0	
								100	72																		
762	[1] 9	110	65	0	0	0				56.4	42.7	76	.0035	3,730	4,940	4,340				10.6	5.5	8.1	3.2	9.8	6.5	79.6	
763	9	110	102	0	0	0				56.7	36.1	64	.0037	3,410	2,000	2,710				9.2	5.0	7.1	3.4	9.5	6.5	93.6	
763	[1] 5	170	75	0	0	0				56.0	40.8	73	.0037	4,490	3,680	4,090				9.9	4.9	7.4	3.1	9.6	6.4	87.2	
764	[1] 7	127	56	0	0	0				54.7	38.4	70	.0035	4,860	4,140	4,500				9.7	5.0	7.4	3.1	9.7	6.4	81.2	
								100	72																		
764	7	127	115	0	0	0				55.3	35.3	64	.0037	3,610	2,070	2,840				8.5	4.3	6.4	3.1	7.6	5.4	86.0	
765	[1] 9	100	37	0	0	0				54.8	39.8	73	.0036	3,610	2,690	3,150				9.8	4.9	7.4	3.0	10.8	6.9	84.8	
	9	100	79	0	0	0				56.3	40.0	71	.0038	5,040	2,260	3,650				9.5	4.4	7.0	3.2	10.4	6.8	92.0	

ROSIN-SIZED PAPERS

781	[1] 7	134	98	0	1.2	0	4.0			57.0	37.4	66	0.0039	3,330	2,530	2,930				8.8	5.0	6.9	3.1	7.9	5.5	88.0	
								100	72	56.3	32.9	59		670	580	630	20	23	22	8.4	4.8	6.6	2.2	6.8	4.5	61.6	
782	[1] 7	150	90	0	.3	0	5.5			56.5	39.4	70	.0036	4,420	5,480	4,950				8.2	5.4	6.8	3.1	8.2	5.7	88.0	
								100	72	56.7	37.1	66		3,600	6,000	4,800	81	110	96	8.5	5.6	7.1	2.8	7.8	5.3	80.8	
783	[1] 7	160	102	2.0	4.0	0	4.0			57.5	37.2	65	.0038	3,080	2,690	2,890				9.2	4.9	7.1	2.5	7.6	5.1	98.4	
								100	72	57.1	34.5	60		1,120	910	1,020	36	34	35	8.5	5.0	6.8	2.2	7.3	4.8	64.0	
766	[1] 7	136	68	2.0	2.0	0	4.4			56.5	37.6	67	.0037	3,670	1,690	2,680				9.1	4.7	6.9	2.6	9.4	6.0	93.2	
								100	72	56.5	36.6	65		2,530	1,060	1,800	69	63	66	9.3	4.9	7.1	3.1	9.2	6.2	76.4	
771	[1] 7	136	78	2.0	1.0	0	5.5			56.2	36.5	65	.0039	3,660	3,290	3,480				9.0	5.4	7.2	2.4	8.3	5.4	86.0	
								100	72	56.0	35.9	64		1,860	2,830	2,350	51	86	69	8.5	5.7	7.1	2.5	7.6	5.1	79.2	
772	[1] 7	136	54	2.0	1.0	0	6.5			57.3	39.8	70	.0039	2,810	3,550	3,180				8.5	5.2	6.9	2.9	8.8	5.9	82.0	
								100	72	57.5	40.7	71		2,450	2,740	2,600	87	77	82	9.0	5.5	7.3	2.7	7.8	5.3	82.8	

STARCH-SIZED PAPERS [4]

792	[1] 7	146	88	0	0.8	0	5.5			56.8	41.5	73	0.0037	5,070	3,890	4,480				9.8	5.5	7.7	2.8	8.3	5.6	118.0	
								100	72	56.5	39.2	69		4,530	3,600	4,070	89	93	91	9.6	5.5	7.6	2.5	8.1	5.3	107.2	
791	[1] 7	147	87	0	.8	4.5	5.5			54.9	49.0	89	.0037	5,880	5,240	5,560				10.0	6.3	8.2	3.2	10.3	6.8	94.8	
								100	72	55.9	48.5	87		4,650	5,020	4,840	79	96	88	10.3	6.2	8.3	3.1	9.1	6.1	92.4	
794	[1] 7	150	100	1.0	3.0	4.5	4.0			55.4	40.6	73	.0037	3,690	4,540	4,120				9.6	5.7	7.7	3.2	8.5	5.9	104.4	
								100	72	54.5	41.9	77		2,030	3,440	2,740	55	76	66	9.3	5.7	7.5	2.8	8.7	5.8	86.0	
793	[1] 7	152	84	1.0	.8	4.5	5.5			56.9	49.5	87	.0037	5,730	4,270	5,000				10.9	6.6	8.8	3.3	9.9	6.6	98.4	
								100	72	56.6	50.4	89		4,570	3,740	4,160	80	88	84	10.7	6.6	8.7	3.1	9.4	6.3	99.6	
821	[1] 7	139	72	0	.5	0	6.0			55.0	39.6	72	.0034	3,990	3,120	3,560				9.8	5.0	7.4	2.8	7.8	5.3	90.6	
								100	72	55.6	42.2	76		4,340	2,640	3,490	109	85	97	9.7	5.2	7.5	2.8	8.5	5.7	91.1	
822	[1] 7	138	68	0	.8	4.5	5.5±			54.9	45.8	84	.0035	4,960	4,120	4,540				10.7	6.0	8.4	3.2	10.0	6.6	80.8	
								100	72	54.9	46.0	84		3,930	3,840	3,890	79	93	86	10.7	5.9	8.3	2.8	9.2	6.0	75.2	
824	[1] 7	133	73	1.0	.5	4.5	5.0			55.7	45.7	82	.0036	4,580	4,040	4,310				9.7	6.2	8.0	2.8	9.4	6.1	92.0	
								100	72	56.9	46.9	83		3,720	4,130	3,930	81	102	92	9.7	5.9	7.8	3.1	8.9	6.0	79.2	

[1] The stock was brushed out in the Jordan.

[2] Approximately pounds per square inch.

[3] Acidity calculated as per cent SO_3.

[4] In runs Nos. 791, 794, and 793 the starch used

ture	Tearing strength			Tearing strength in per cent of initial			Opacity	Sizing quality		Chemical tests										
										Sizing materials present			Acidity							
Aver-age	Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average		Indicator (21° C.)	Curl (21° C.)	Ash	Rosin	Starch	Fiber extract (Kohler-Hall method)	Fiber suspension	Fiber extract	Alpha cellulose content	Alpha cellulose content corrected for sizing materials	Decrease in alpha cellulose content on heating	Copper number	Increase in copper number on heating
Per cent	*g*	*g*	*g*	*Per cent*	*Per cent*	*Per cent*		*Seconds*	*Seconds*	*Per cent*	*Per cent*	*Per cent*	*Per cent* [3]	*Per cent* [3]	*pH*	*Per cent*	*Per cent*	*Per cent*		
7.0	81.6	72.4	77.0				73.6			0.20	0.2				6.6	91.3	91.5		0.65	
6.6	84.4	83.2	83.8	103	115	109										90.8		0.5	.79	0.14
6.8	94.4	78.8	86.6				74.8			.16	.2					91.2	91.4		.67	
6.9	97.2	75.2	86.2	103	95	99										90.9		.3	.80	.13
6.1	89.6	79.2	84.4				76.2									91.3	91.5		.65	
6.1	92.4	85.2	88.8	103	108	106										90.9		.4	.80	.15
5.9	106.0	86.8	96.4				78.2			.24	.2					91.6	91.8		.65	
																91.1		.5	.80	.15
6.5	79.6	90.8	85.2				77.0													
6.5	93.6	104.4	99.0				77.8													
6.4	87.2	96.0	91.6				78.5			.27	.2									
6.4	81.2	95.2	88.2				77.0			.21	.2					91.5	91.7		.63	
																91.1		.4	.74	.11
5.4	86.0	92.0	89.0				78.8													
6.9	84.8	83.6	84.2				75.7													
6.8	92.0	100.0	96.0				77.0													
5.5	88.0	86.8	87.4				79.5			0.35	0.1		0.092	0.196	3.8	89.9	90.0		0.72	
4.5	61.6	56.4	59.0	70	65	68										87.0		3.2	.92	0.20
5.7	88.0	90.4	89.2				79.0			.42	.2		.016	.076	4.9	90.3	90.5		.67	
5.3	80.8	79.6	80.2	92	88	90										89.9		.4	.81	.14
5.1	98.4	108.0	103.2				80.4	14.7	22.6	.52	1.8		.116	.244	3.7	87.5	89.1		.99	
4.8	64.0	65.2	64.6	65	60	63										81.7		6.6	1.59	.60
6.0	93.2	99.2	96.2				79.1	17.6	27.5	.45	1.9		.068	.192	4.2	88.4	90.1		1.06	
6.2	76.4	72.4	74.4	82	73	78										84.9		4.0	1.59	.53
5.4	86.0	103.2	94.6				81.1	15.9	20.0	.51	2.3		.016	.060	5.2	88.7	90.8		.84	
5.1	79.2	92.4	85.8	92	90	91										87.5		1.4	1.21	.37
5.9	82.0	98.8	90.4				81.2	14.3	17.5	.57	1.9		.010	.040	5.4	88.3	90.0		.91	
5.3	82.8	88.4	85.6	101	90	96										87.6		.8	1.19	.28
5.6	118.0	121.6	119.8							0.35	0.2		0.014	0.051	5.2	90.1	90.3		0.74	
5.3	107.2	114.4	110.8	91	94	93										88.9		1.3	.93	0.19
6.8	94.8	111.2	103.0							.30	.2	2.10	.017	.041	5.5	88.9	90.3		.69	
6.1	92.4	97.6	95.0	98	88	93										88.1		.9	.80	.11
5.9	104.4	108.8	106.6				77.8	16.7	21.6	.32	.9	2.26	.072	.157	4.2	86.7	88.8		1.05	
5.8	86.0	97.2	91.6	82	90	86										84.9		2.1	1.44	.39
6.6	98.4	110.4	104.4					11.1	21.5	.32	1.1	2.34	.028	.054	5.0	88.2	90.6		.89	
6.3	99.6	104.4	102.0	101	95	98										87.0		1.4	1.10	.21
5.3	90.6	81.8	86.2				76.8			.49	.2		.019	.057	5.3	91.2	91.4		.71	
5.7	91.1	78.4	84.8	101	96	99										90.8		.4	.76	.05
6.6	80.8	76.0	78.4				76.5			.36	.2	1.47	.011	.044	5.6	89.5	90.8		.66	
6.0	75.2	58.0	66.6	93	76	85										89.2		.3	.75	.09
6.1	92.0	86.0	89.0				78.8	7.9	6.5	.33	1.0	1.02	.023	.084	4.9	89.0	90.8		.72	
6.0	79.2	70.8	75.0	86	82	84										88.3		.8	.82	.20

[3] The starch used was prepared by an acid process. In runs Nos. 822 and 824 an oxidation process starch was used.

(2) EFFECT OF BEATING ON THE ALPHA CELLULOSE CONTENT AND COPPER NUMBER.—A 2 per cent suspension of fibers was beaten in a small beater. Portions of the stock were taken out at the following intervals: (1) After a few minutes of beating, (2) after 2½ hours of beating, (3) after 5 hours of beating, and (4) after 7½ hours of beating. Hand sheets were made from each of these portions. The alpha cellulose content and copper number were determined on squares of the sheets and also on the ground material. The data obtained, which are presented in Table 2, indicate that the beating caused practically no change in the chemical properties of the fibers measured by these tests.

TABLE 2.—*Effect of beating on the alpha cellulose content and copper number.*[1]

Sample	Duration of beating	Alpha cellulose content		Copper number	
		¼-inch squares of hand sheet	Ground fiber	¼-inch squares of hand sheet	Ground fiber
	Hours	*Per cent*	*Per cent*		
1	0	93.7	91.4	0.49	0.65
2	2½	94.4	90.7	.49	.63
3	5	94.8	90.8	.50	.64
4	7½	95.3	90.7	.51	.62

[1] The beating was done in a laboratory beater.

(*b*) MACHINE-MADE PAPER

Table 3 gives data relative to the operation of the beater and the test results of the machine-made papers.

The results indicated that a 7-hour beating, with the method of roll manipulation found most suitable, would give a satisfactory balance of the various desired properties in the paper. A light jordanning of the beaten stock appeared to be of advantage. This interval of beating offers a sufficient time for the gradual and proper brushing out of the fibers to be accomplished before excessive "hydration" has taken place. In Figure 3 a photomicrograph is shown of fibers beaten seven hours. The jordanned stock is shown in Figure 4. These photomicrographs show this fiber may be satisfactorily fibrillated and frayed if properly beaten. An outline of the beating procedure selected as suitable for this type of fiber is given in Table 4. This procedure was used for all subsequent runs.

In regard to the stability of the unsized paper, it appears that these papers are almost entirely resistant to treatment at 100° C. for 72 hours. Under these conditions there is a very slight decrease in the alpha cellulose content, a correspondingly slight increase in the copper number, and practically no change in the strength properties. No appreciable yellowing of the paper occurs. These are considered favorable indications of permanence. Tests of commercial papers made from less pure fibers show that they may lose practically all their initial folding endurance and decrease as much as 8 per cent in alpha cellulose content on heat treatment.

TABLE 4.—*Schedule of roll settings for beating*

Beating interval		Position of roll [1]	Beating interval		Position of roll [1]
Hours	*Minutes*		*Hours*	*Minutes*	
0	0	10	2	30	½
0	15	10	3	0	0
0	30	4	4	0	0
1	0	2	5	0	0
1	30	1½	6	0	−½
2	0	1	7	0	−½

[1] Indicated as turns of the hand wheel with which the position of the roll relative to the bed plate is changed. At the −½ setting the roll impinges on the bedplate, and at the zero setting the bedplate is just barely cleared. One turn of the hand wheel raises or lowers the roll 0.008 inch.

2. BEATER SIZED PAPERS

(a) ROSIN-SIZED

The necessity for employing minimum amounts of rosin and alum in the sizing of papers intended for permanent use is now generally recognized. The machine runs described below were made for the purpose of studying the effect of rosin sizing, particularly the acidity of rosin-sized papers. Each of four papers was sized with 2 per cent rosin, while the amounts of alum used to precipitate the size were varied from 1 per cent, based on weight of fiber, to 4 per cent. The duration of beating and other factors were kept constant as far as possible. Two control runs were made in which the amounts of alum added to the stock were varied, but in which no rosin was employed. Table 3 contains the data relative to the beating interval, sizing of the stock, and tests of the machine-made papers.

In run No. 783 a large excess of alum over that required for adequate sizing was purposely added. The finished paper, which had a pH of 3.7, discolored appreciably and underwent marked changes in strength and chemical properties when subjected to the accelerated aging test. The unsized paper of run No. 781, which corresponded to run No. 783 in all respects except that no rosin size was present, was on the whole much more stable and discolored but slightly on heating, indicating that rosin sizing may contribute a deteriorative effect in addition to that of the acid.

In run No. 766, only one-half the amount of alum used in the previous run was employed, with a resulting improvement in stability. The pH of this paper was 4.2. The amount of alum used was still further reduced in runs Nos. 771 and 772. These papers had pH values of 5.2 and 5.4, respectively, and were found to be very stable toward accelerated aging. While the former was satisfactorily sized, the latter was somewhat deficient in this respect. Therefore, under the existing conditions, the optimum pH value combining high stability with adequate sizing appears to be approximately 5.0.

In general the agreement between the pH values of stock at the head box and extracts of the finished paper was fairly good. The widest discrepancies occurred in the case of the more nearly neutral papers. In the case of run No. 772 the pH of the stock at the head box was 6.5, while that of the extract of finished paper was 5.4. This wide difference is probably due to the fact that in the measurement of the pH of the head-box stock the unadjusted rather than the isohydric type of indicators was used.

FIGURE 3.—*Highly purified wood fiber,* $\times$ *100*

After completion of beating (7 hours). Before jordanning.

FIGURE 4.—*Highly purified wood fiber,* $\times$ *100*

After completion of beating (7 hours). After jordanning.

Data on the series of rosin-sized papers indicate the importance of acidity control when the combined properties of high stability and good writing quality are desired. The findings are in accord with previous experience in the bureau mill as to the correct acidity for optimum sizing results. [18]

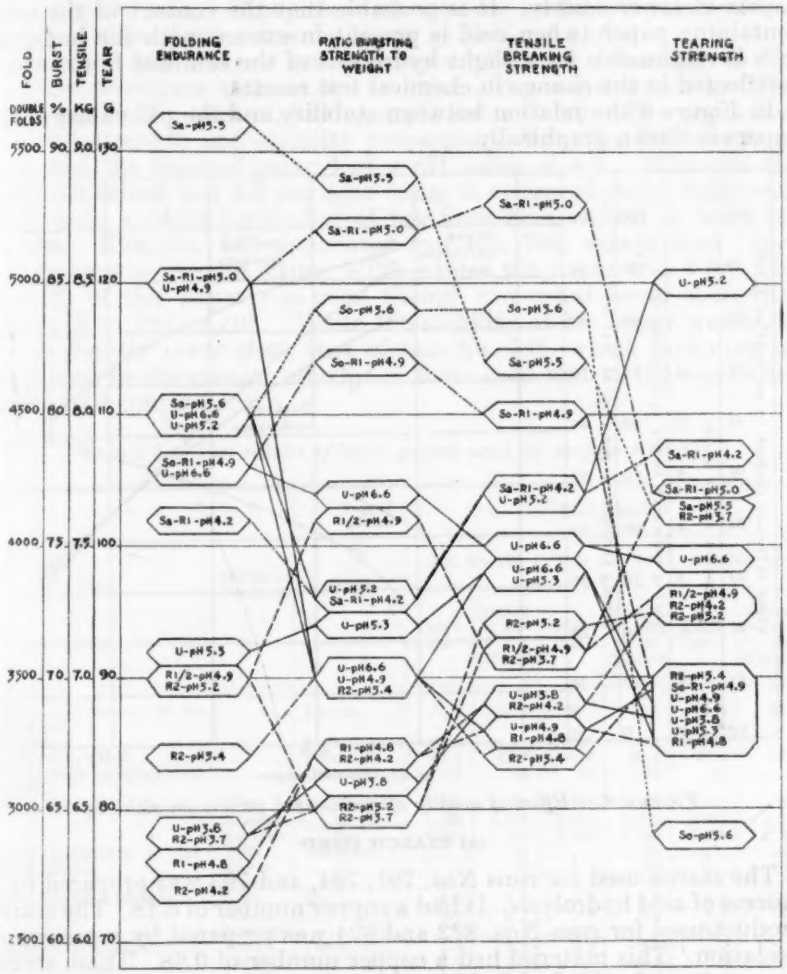

FIGURE 5.—*Strength properties of unsized and beater-sized papers*

KEY

U....Unsized.
R....Rosin sized. Number following indicates per cent rosin used.
Sa...Starch sized. Starch prepared by acid process.
So...Starch sized. Starch prepared by oxidation process.

——— Unsized.
– – – – Rosin sized.
..... Starch sized.
—·—·— Rosin and starch sized

The amount of rosin used in sizing was chosen arbitrarily. Other experiments made with a view to determining the minimum required

[18] M. B. Shaw, Hydrogen Ion Concentration in the Paper Mill, Paper Trade Jour., vol. 81, No. 10, pp. 93–96, Sept. 3, 1925.

amount of rosin indicate that the 2 per cent used was considerably greater than that actually required to effectually size this fiber.

In general the rosin-sized papers had somewhat less strength than the unsized papers. The initial alpha cellulose content was slightly lower and the copper number slightly higher than those of the unsized papers. These differences are much less apparent in the case of the papers of lower acidity. It is probable that the contact of the acid-containing paper (when acid is present in excess) with the hot drier rolls is responsible for a slight hydrolysis of the cellulose fibers which is reflected in the change in chemical test results.

In Figure 6 the relation between stability and the pH values of the papers is shown graphically.

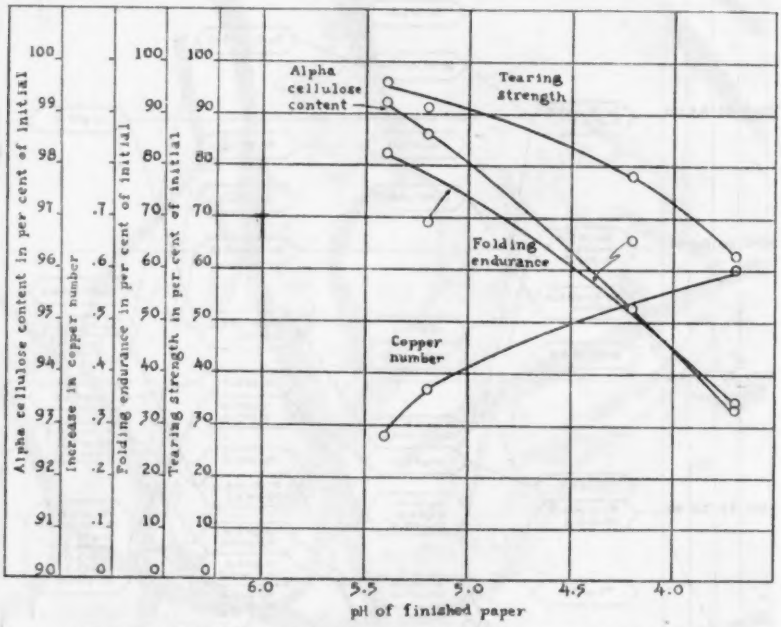

FIGURE 6.—*Effect of acidity of rosin-sized papers on stability*

(*b*) STARCH SIZED

The starch used for runs Nos. 791, 794, and 793 was prepared by a process of acid hydrolysis. It had a copper number of 0.18. The starch product used for runs Nos. 822 and 824 was prepared by a process of oxidation. This material had a copper number of 0.68. These starch runs were made chiefly for the purpose of studying the effect of beater starch on the properties of the papers. No complete study of starch sizing itself was intended at this time. In general beater sizing with starch increased the bursting strength and folding endurance, and decreased the tearing strength of the paper. The presence of starch had no adverse affect upon the stability of the papers, and in several cases apparently effected a slight improvement in this respect. Table 3 contains the data relative to the beating interval, sizing of the stock, and tests of the machine-made papers.

The retentions of starch in the papers varied from about 25 to 50 per cent.

3. SURFACE-SIZED PAPERS

(a) BOND TYPE

(1) BASIC PAPERS USED FOR SURFACE SIZING.—Three different basic papers were employed in the study of the effect of surface sizing on the properties of the papers. Following are described the machine-made papers used. Complete data relative to the preparation and testing of these papers may be found in Tables 5 and 6.

Run No. 785 was an unsized paper prepared according to the standard procedure without the addition of rosin size or alum. The paper was nearly neutral, having a pH value of 6.6. The paper had excellent strength and stability properties. Run No. 796 was rosin sized and the finished paper had a pH value of 4.9. Although the paper contained but 0.5 per cent rosin, it appeared to be fairly well sized, only a slight feathering of ink lines being noted in some instances. Run No. 787 duplicated run No. 796, except that 1 per cent rosin was used in sizing. The pH of the paper was 4.8. The strength of this paper was good though somewhat lower than that of runs Nos. 785 or 796. While the stability of the paper was high, it was slightly lower than that of run No. 796, which fact may be attributed to the greater amount of rosin used and to the somewhat higher acid content.

TABLE 5.—*Test results of basic papers used for surface sizing* [1]

Item	Machine direction	Units	Basic paper					
			Run No. 785		Run No 796		Run No. 787	
			Original	Heated at 100° C. for 72 hours	Original	Heated at 100° C. for 72 hours	Original	Heated at 100° C. for 72 hours
Weight (500 sheets, 25 by 40 inches).		Pounds	56.8	57.0	55.3	54.8	55.4	54.9
Thickness		Inch	0.0038		0.0036		0.0038	
Bursting strength		Points [2]	43.6	42.7	41.8	42.6	37.3	38.4
Ratio of bursting strength to weight.		Per cent	77	75	76	78	67	70
Folding endurance	With	Double folds	3,990	3,880	3,710	3,180	2,960	2,280
	Across	do	4,500	4,470	3,300	2,810	2,540	2,270
	Average	do	4,250	4,180	3,510	3,000	2,750	2,280
Folding endurance in per cent of initial.	With	Per cent		97		85		77
	Across	do		99		86		89
	Average	do		98		86		83
Tensile breaking strength	With	Kg	9.2	9.1	8.8	9.0	8.5	8.4
	Across		5.8	5.7	5.3	5.3	5.2	5.2
	Average		7.5	7.4	7.1	7.2	6.9	6.8
Elongation at rupture	With	Per cent	2.7	2.8	2.8	2.8	2.7	2.8
	Across		7.7	7.7	7.7	7.9	7.8	7.9
	Average		5.2	5.2	5.3	5.3	5.3	5.4
Tearing strength	With	g	96.1	88.2	96.4	85.6	93.1	86.6
	Across		101.3	94.9	99.4	90.4	99.8	85.5
	Average		98.7	91.5	97.9	88.0	96.4	86.1
Tearing strength in per cent of initial.	With	Per cent		92		89		93
	Across			94		91		86
	Average			93		90		90

[1] The data were composited from the values given in Table 6.
[2] Approximately pounds per square inch.

(2) SURFACE-SIZING BATHS.—A brief description is given below of the different solutions used in surface sizing.

(*a*) A 4 per cent solution of glue having a pH value of 6.0.

(*b*) A 4 per cent solution of glue to which 7 per cent alum (based on the weight of glue) was added. This solution had a pH value of 4.2.

(*c*) A 4 per cent solution of glue to which one-fourth per cent formaldehyde (based on the weight of glue) was added. The pH of this solution was 5.5.

(*d*) A 4 per cent starch solution having a pH of 7.3. The starch product used was specially prepared for surface sizing by a process of acid hydrolysis. It had a copper number of 0.61.

(*e*) This solution was the same as (*d*), except that it contained 2 per cent alum (based on the weight of starch). The pH of the solution was 5.4.

(*f*) A 4 per cent starch solution having a pH of 7.2. The starch product used was specially prepared for surface sizing by an oxidation process. The starch had a copper number of 0.94.

(*g*) This solution was the same as (*f*), except that it contained 2 per cent alum (based on the weight of starch). The pH of the solution was 4.6.

Complete data on the various surface-sizing runs, together with the test results obtained on the sized papers, are given in Table 6.

Control samples corresponding to each of the surface-sizing runs were tested individually for strength and stability. These control samples were taken immediately before and after each surface-sizing treatment so as to be as representative as possible of the portion of paper sized. In the case of runs Nos. 185 to 189 inclusive, however, one sample of the basic paper, taken before and after each pair of sizing treatments made with and without alum present in the starch solution, served as a control sample for both runs. A composite of the results on all the control samples of basic papers makes up the data which are presented in Table 5. In Table 6 are given the data which were obtained on the individual control samples together with those which were obtained on the corresponding surface-sized papers.

In general, surface sizing with glue or starch resulted in marked increases in bursting strength, tensile breaking strength, elongation, and folding endurance. The tearing strength alone underwent a decrease. With the exception of the folding endurance the magnitude of the various strength changes was roughly in proportion to the absorbency of the basic paper, or to the amount of glue or starch taken up by the sheet. These changes are shown graphically in Figures 7a and 7b.

All the papers of the series were of exceptionally high stability, as regards the resistance of such properties as folding endurance, tearing strength, alpha cellulose content, and copper number to the effects of the heat treatment to 100° C. for 72 hours. In all cases upwards of 80 per cent of the initial folding endurance was retained after heat treatment. Papers surface sized with glue or starch containing alum were found to be no less stable than in corresponding cases where alum was not present in the sizing bath. This points to the relative harmlessness of surface acid. Apparently as pointed out by Kohler and Hall,[16] all acid present in paper is not necessarily harmful. The data indicate that evidence as to harmful acidity which is based on estimates of total acidity, or on the pH values of aqueous

[16] See footnote 9, p. 769.

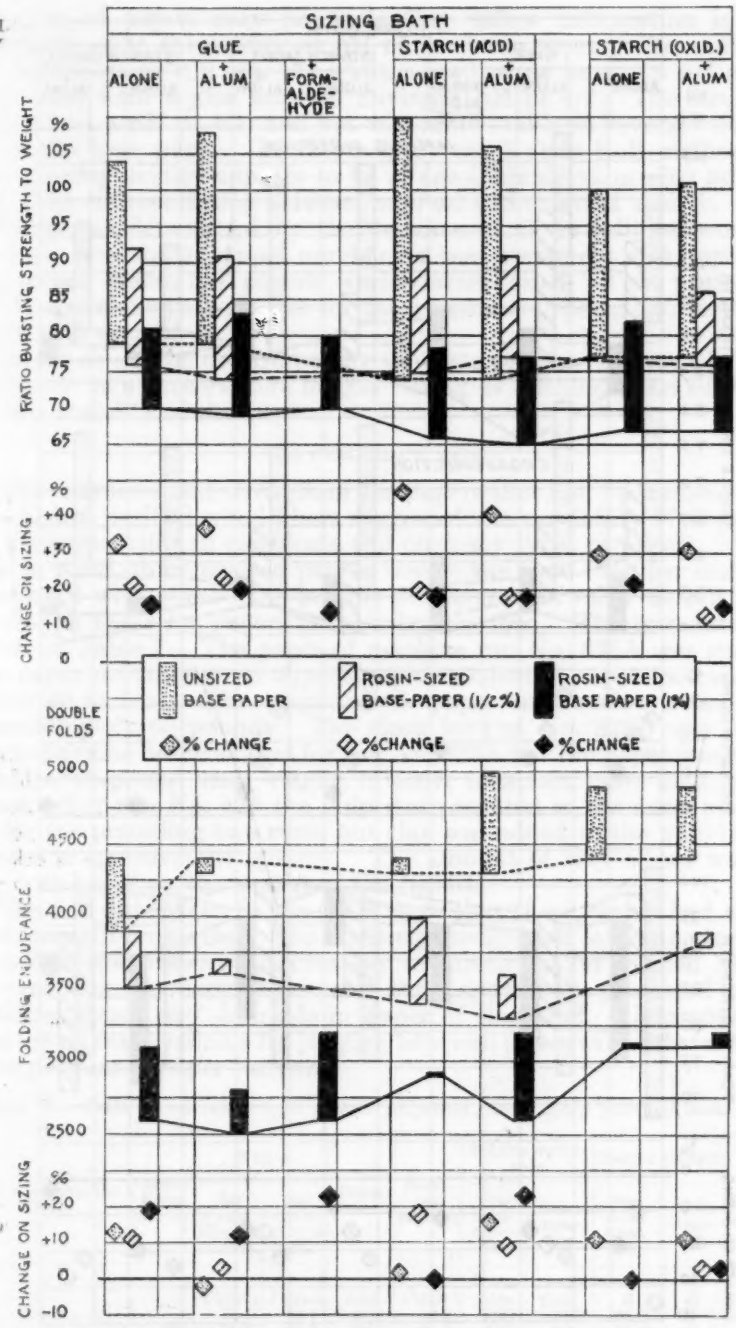

FIGURE 7a.—*Effect of surface sizing on the strength of papers*

The strength values of basic papers and surface-sized papers are indicated by the heights (read on the scale) of the upper and lower ends of the bars. The total length of each bar thus shows the change due to surface sizing. The bars are connected by pattern lines. These show the initial values.

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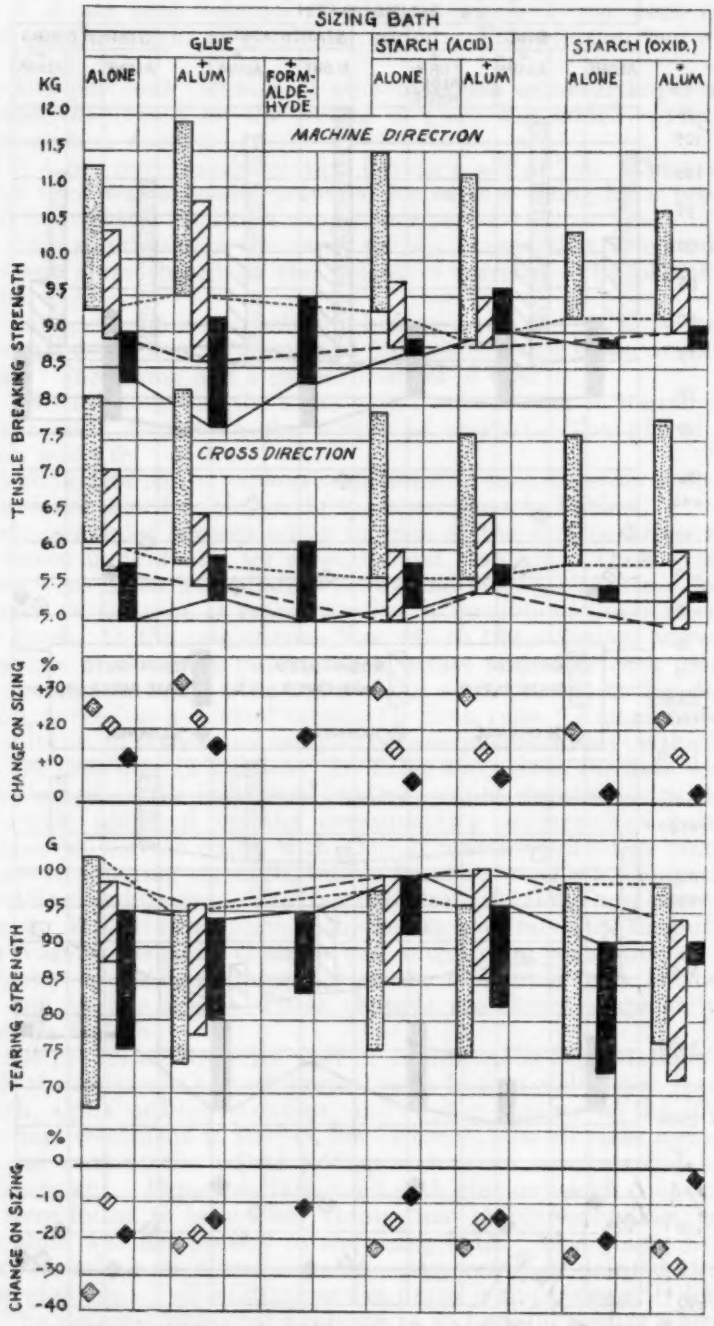

FIGURE 7b.—*Effect of surface sizing on the strength of papers*

The strength values of basic papers and surface-sized papers are indicated by the heights (read on the scale) of the upper and lower ends of the bars. The total length of each bar thus shows the change due to surface sizing. The bars are connected by pattern lines. These show the initial values.

extracts of paper, may be misleading unless information is also available as to the acidity or pH of the basic paper. For example, in surface-sizing run No. 174 a rosin-sized paper having a pH of 4.8 was sized with a glue solution having a pH of 4.2. The resultant paper had a pH of 4.4, and yet was more stable in several respects than the base paper. In this respect the Kohler-Hall method for determining acidity appears to be of considerable value also as they state, for differentiating between internal and external acidity. The stability, as determined by the decrease in alpha cellulose content and the increase in copper number on heat treatment was improved somewhat when the papers were surface sized. This protective effect was somewhat greater for the glue-sized papers than for those sized with starch.

As far as can be determined by the tests applied, the use of formaldehyde as a preservative in glue sizing is without marked effect on the stability of the paper.

(*b*) CURRENCY TYPE

The character and strength of the papers that had been made from the highly purified wood fibers suggested the possibility of their use in the preparation of certificate and currency types of papers. With this in mind, three unsized papers were made from the fiber and surface sized with glue. The beating procedure and other details were similar to those for papers previously described. The test data are given in Table 7. The paper of machine run No. 825A was run off the paper machine as an approximately 61-pound paper (500 sheets, 25 by 40 inches). The weight of the paper after surface sizing was approximately 63 pounds. The stock for run No. 825B was taken from the same batch as that for run No. 825A but the paper was made heavier, 68-pound basis weight, in order to obtain more bulk in the sheet. For run No. 826 the pulp was prepared in the same manner as for the preceding two runs, but clay was added to the pulp in the beater to improve the opacity. The amount of clay added was 10 per cent based on the weight of the furnish.

The test data given in the table show that these papers had excellent strength properties. The bursting strength and folding endurance exceeded the present specification requirements for United States Government currency paper and they apparently possessed other qualities considered desirable in paper of this kind. Unfortunately there is no test available for judging how well paper will withstand the wear peculiar to paper currency.

TABLE 7.—*Data on currency type papers prepared from highly purified wood fibers*

Paper machine run No.	Surface sizing run No.	Weight		Thickness	Bursting strength	Folding endurance		Tearing strength		Opacity
		500 sheets, 17 by 22 inches	500 sheets, 25 by 40 inches			Machine direction	Cross direction	Machine direction	Cross direction	
		Pounds	*Pounds*	*Inch*	*Points*[1]	*Double folds*	*Double folds*	*G*	*G*	
825A		22.7	60.7	0.0040	44.8	4580	7270	81.4	93.6	79.7
	190	23.4	62.6	.0038	63.2	3960	5400	80.8	84.8	77.3
825B		25.3	67.8	.0042	49.5	5200	5940	110.6	109.0	82.5
	191	26.2	70.1	.0041	68.0	4280	5950	91.6	93.2	79.1
826		22.6	60.3	.0038	38.8	3870	1980	96.2	89.2	85.3
	192	23.7	63.5	.0037	55.5	3640	3250	78.8	74.4	82.7

[1] Approximately, pounds per square inch.

VII. CONCLUSIONS

1. High-grade bond papers were made from highly purified wood fibers by the following procedure, which was found to give the best results with the fibers under study. The beating of the stock was conducted in such a manner as to minimize cellulose gel formation, and yet obtain the desired fraying out and fibrillation of the individual fibers. This was satisfactorily accomplished by means of a 7-hour beating, during the course of which the roll was very gradually lowered. The beaten stock was lightly brushed in the Jordan.

2. When so beaten the strength exceeded that required by the Government for the highest grade writing papers; and for currency type paper the strength requirements for United States currency were exceeded.

3. The stability of rosin-sized papers in the accelerated aging test was seriously impaired by the presence of excess alum, but with the control of acidity at pH 5.0 a highly stable, well-sized paper was produced.

4. Starch used as sizing by addition in the beater did not reduce the stability in the aging test.

5. Surface sizing with glue or starch improved the resistance to the aging test, especially with glue sizing.

6. Moderate amounts of alum (used as a preservative for glue or starch in the surface sizing baths) were found not deleterious.

VIII. ACKNOWLEDGMENT

The authors are indebted to M. J. O'Leary [17] and G. O. Stone [18] who assisted in these studies.

WASHINGTON, August 25, 1931.

[17] Assistant paper maker.

[18] Assistant research associate.

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PRELIMINARY NOTE ON AN AUTOMATIC RECORDER GIVING A CONTINUOUS HEIGHT RECORD OF THE KENNELLY-HEAVISIDE LAYER

By T. R. Gilliland and G. W. Kenrick

ABSTRACT

This paper describes a preliminary installation of a continuous automatic recorder of virtual heights of the Kennelly-Heaviside layer. This installation requires that a chopper at the transmitter and a revolving mirror at the receiving station be driven by synchronous motors connected to the same power system. The group retardation method of Breit and Tuve is used with a few modifications which permit continuous records to be made. Suggestions are made for improvements which might be incorporated in a permanent installation.

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I. INTRODUCTION

During the last few years measurements of the virtual height of the Kennelly-Heaviside layer have commanded no little interest and numerous papers have been published describing such observations. In America most of the workers have employed the group retardation or pulse method originated by Breit and Tuve in making the measurements reported.[1,2,3]

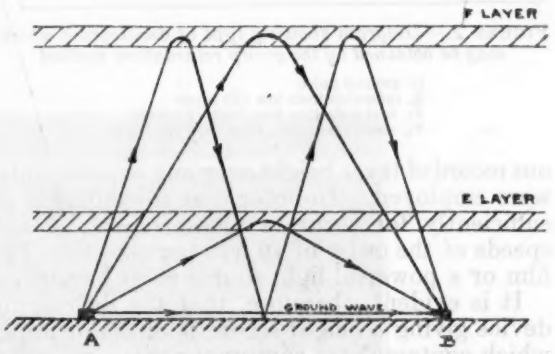

FIGURE 1.—*Diagram showing various paths by which pulse may arrive at receiving station*

The principle employed in this method may be understood by reference to Figures 1 and 2. A very short pulse or dot is transmitted from point A and may arrive at point B by several paths as indicated in Figure 1. The pulses arriving at the receiver over the ground and along the several paths

[1] See Breit and Tuve, Physical Rev., vol. 21, pp. 554–576, 1926; Proc. I. R. E., vol. 16, pp. 1236–1239. Heising, R. A., Proc. I. R. E., vol. 16, pp. 75–99. de Mars, Gilliland, and Kendrick, Proc. I. R. E., vol. 19, pp. 106–113.

[2] For other methods see Appleton, E. V., Proc. Royal Soc., vol. 109, p. 621, 1925; vol. 113, p. 450, 1926; vol. 115, p. 291, 1927; vol. 117, p. 576; 1928.

[3] For other American methods see Mirick & Hentschell, Proc. I. R. E., vol. 17, pp. 1034–1041.

result in several pulses at the receiver for each transmitted pulse. If the output of the receiving set is led to an oscillograph, a record similar to that shown in Figure 2 may be obtained. Figure 3a is an actual oscillogram obtained by this method showing pulses which have arrived by several paths, while Figure 3b shows the ground pulse and only one reflection. If the oscillograph film speed is known, the time interval between the arrival of the ground pulse and any of the reflected pulses may be measured, and from this the virtual height of the layer may be computed.

The major difficulty with the method described above, and one which is common to most methods so far reported, is that each oscillogram taken gives the virtual height only over a brief period, usually a fraction of a second. In order to obtain a clear idea of the variation of the layer height over a considerable period, such as 24 hours for instance, it is necessary for the observer to remain at the apparatus and take frequent oscillograms, each of which gives him but a single point on his desired curve of virtual height as a function of time. Such observations hence require considerable resources in personnel and supplies (notably film) when more than a few fragmentary measurements are to be made. In fact, several hundred feet of film are usually required for a 24-hour run, and as the labor of subsequent development and measurement of the oscillograms taken is considerable it is probable that the entire time of no less than six workers would be necessary to secure a continuous record of layer height over any considerable period if such methods were employed. In order that the different pulses may be separated sufficiently for accurate measurement, it is necessary to use film speeds of the order of 10 feet per second. This means that sensitive film or a powerful light source must be used.

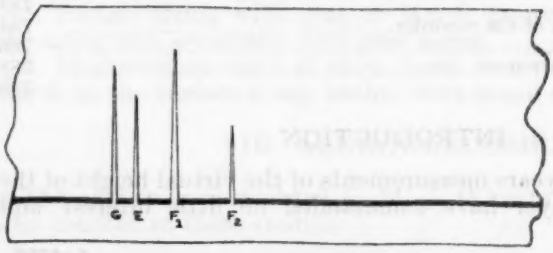

FIGURE 2.—*Diagram showing type of oscillogram which may be obtained by the group retardation method*

G, ground pulse.
E, reflection from low (E) layer.
F_1, first reflection from high (F) layer.
F_2, second reflection from high (F) layer.

It is evident, therefore, that the development of some automatic device giving a height record is of major importance to any program which contemplates continuous measurements of layer height. This paper describes a preliminary set-up which has proven the practicability of a scheme for making continuous height records, and improvements are suggested which might be incorporated in a permanent installation.

II. PRINCIPLE OF OPERATION OF THE RECORDER

With a few modifications, the group retardation method as described above may be used to give continuous automatic records. The general scheme may be best understood by reference to Figure 4. The pulses are sent out from a transmitter which is keyed by a chopper

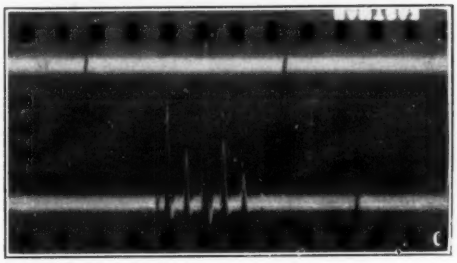

FIGURE 3a.—*Actual oscillogram obtained by group retardation method showing impulses which have arrived by several paths*

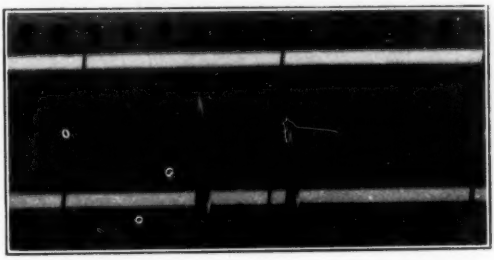

FIGURE 3b.—*Oscillogram showing ground pulse and one reflection*

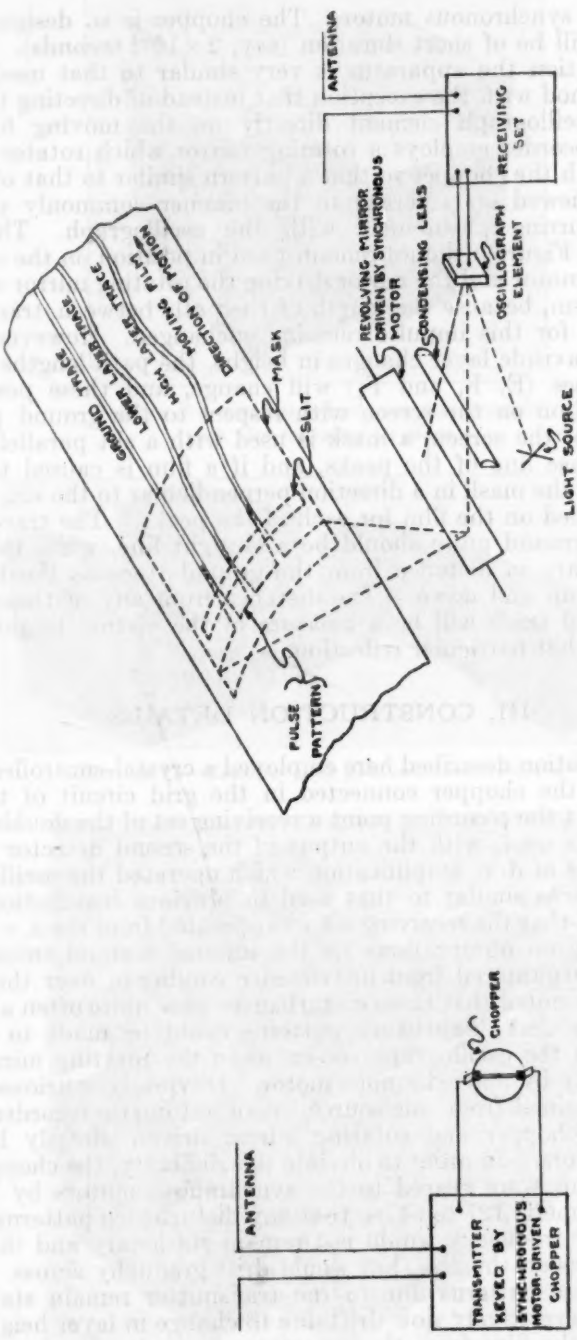

FIGURE 4.—*Schematic diagram of system used with automatic Kennelly-Heaviside layer height recorder*

driven by a synchronous motor. The chopper is so designed that the pulses will be of short duration (say, 2×10^{-4} seconds). At the receiving station the apparatus is very similar to that used in the original method with the exception that instead of directing the light from the oscillograph element directly on the moving film, the automatic recorder employs a rotating mirror which rotates in synchronism with the chopper so that a pattern similar to that of Figure 2 may be viewed on a screen in the manner commonly used for viewing recurring phenomena with the oscillograph. The peak marked *G* in Figure 2 should remain fixed in position on the screen if the chopper motor and the motor driving the rotating mirror are kept in synchronism, because the length of the path between transmitter and receiver for this impulse remains unchanged. However, if the Kennelly-Heaviside layer changes in height, the path lengths for the other impulses (E, F_1 and F_2) will change, and these peaks will shift in position on the screen with respect to the ground peak *G*. If, in place of the screen, a mask is used with a slit parallel to and above the base line of the peaks, and if a film is caused to move slowly across the mask in a direction perpendicular to the slit, a trace will be recorded on the film for each of the peaks. The trace representing the ground pulse should be a straight line, while the other traces will vary in distance from the ground trace as the layer or layers move up and down. The distance from any of these traces to the ground trace will be a measure of the virtual height corresponding to that particular reflection.

III. CONSTRUCTION DETAILS

The installation described here employed a crystal-controlled transmitter with the chopper connected in the grid circuit of the first amplifier. At the recording point a receiving set of the double-detection type was used, with the output of the second detector feeding into one stage of d. c. amplification which operated the oscillograph. The system was similar to that used in previous installations with the exception that the receiving set was operated from the a. c. mains.

In carrying on observations by the original method trouble was frequently encountered from interference coming in over the power lines. It was noted that these disturbances were quite often at power frequency, so that disturbance patterns could be made to remain stationary on the oscillograph screen when the rotating mirror was driven directly by a synchronous motor. Obviously spurious results would be obtained from this source by an automatic recorder which employed a chopper and rotating mirror driven directly by synchronous motors. In order to obviate this difficulty, the chopper and rotating mirror were geared to the synchronous motors by an odd gear ratio, namely, 127 to 64, so that any disturbance patterns occurring at power frequency would not remain stationary and thus give spurious traces on the film, but would drift gradually across. However, the pulse patterns due to the transmitter remain stationary except for the relatively slow drift due to change in layer height, and the light on the film from these patterns is predominant over that from sources of disturbance.

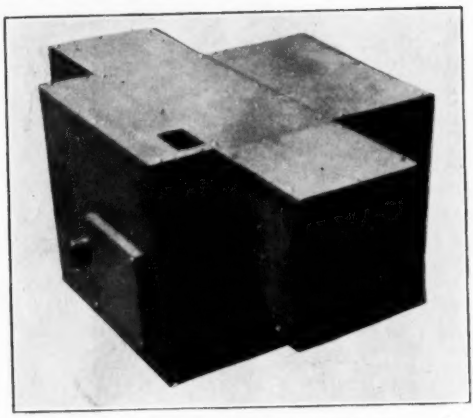

FIGURE 6.—*Photograph of complete recorder with film container in place*

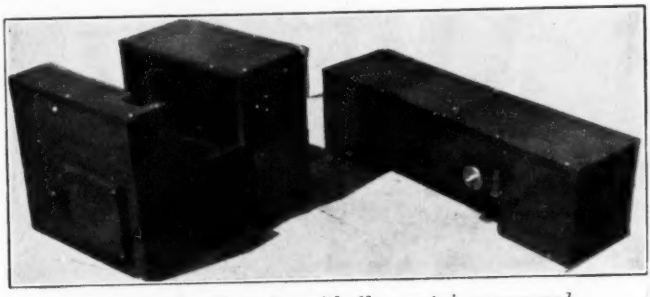

FIGURE 7.—*Recorder with film container removed*

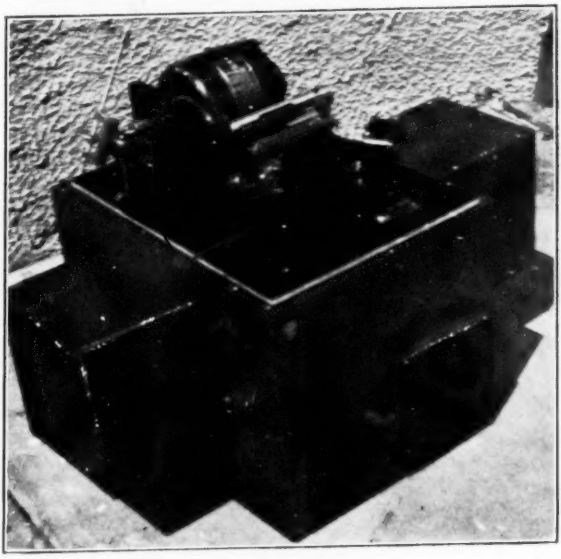

FIGURE 8.—*Photograph of synchronous motor, rotating mirror, oscillograph element, and lamp*

The gears for driving the film are shown at the left.

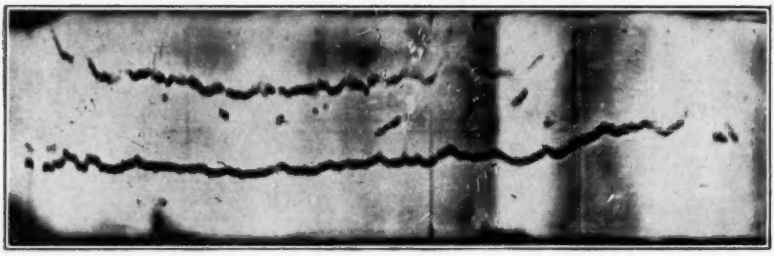

FIGURE 9.—*Example of height record showing gradual rise of layer from 241 km to 399 km*

Note also temporary appearance of other layers. Record runs from 5.30 p. m. to 2.15 a. m., June 13, 1931. Frequency 4,045 kc. Ground trace appears at bottom of record.

The film was driven through a system of gears by the same synchronous motor used for driving the rotating mirror. A film speed of 2.5 feet per 24 hours was used. A six-volt automobile lamp bulb was employed as a light source for the oscillograph. Figure 5 is a drawing of the assembly with film drive and film container omitted. Figure 6 is a photograph of the complete recorder with film container in place. Figure 7 shows the film container removed while Figure 8

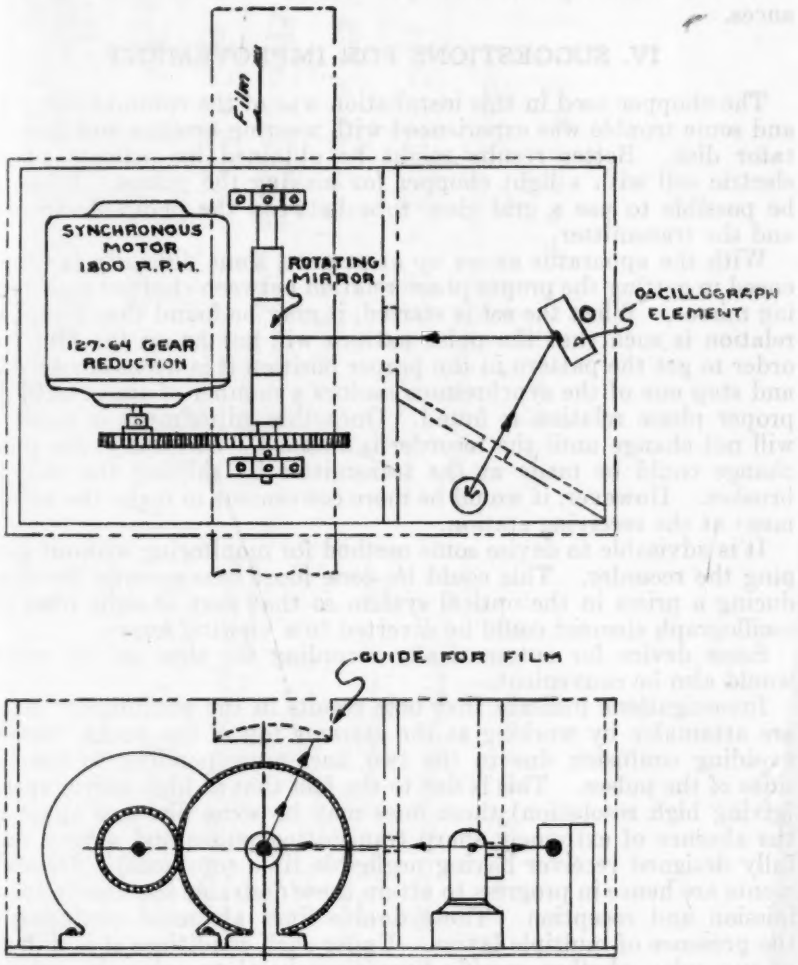

FIGURE 5.—*Drawing of assembly of recorder with film drive and film container omitted*

is a photograph of the synchronous motor, rotating mirror, oscillograph element, and lamp. The gears for driving the film are shown at the left.

Figure 9 is a typical record which shows the variation in height over a period of 8¾ hours. The frequency was 4045 kc and the distance from transmitter to receiver was 3 miles.

The advantages of this system may be enumerated as follows:

1. It gives a continuous automatic record.
2. It requires only a small fraction of the amount of film used by other methods. A less sensitive film and weaker light source may be used.
3. It requires little attention.
4. It will record heights of two or more layers simultaneously.
5. It is relatively free from power line and atmospheric disturbances.

IV. SUGGESTIONS FOR IMPROVEMENT

The chopper used in this installation was of the commutator type, and some trouble was experienced with wearing brushes and commutator disk. Better results might be obtained by using a photo-electric cell with a light chopper for making the pulses. It should be possible to use a grid glow tube between the photo-electric cell and the transmitter.

With the apparatus as set up at present, some difficulty is experienced in getting the proper phase relation between chopper and rotating mirror. When the set is started, it may be found that the phase relation is such that the pulse pattern will not be on the film. In order to get the pattern in the proper position it is necessary to start and stop one of the synchronous motors a number of times until the proper phase relation is found. Once this adjustment is made, it will not change until the recorder is stopped. Obviously, the phase change could be made at the transmitter by shifting the chopper brushes. However, it would be more convenient to make the adjustment at the receiving station.

It is advisable to devise some method for monitoring without stopping the recorder. This could be done most conveniently by introducing a prism in the optical system so that part of light from the oscillograph element could be diverted to a viewing screen.

Some device for automatically recording the time on the record would also be convenient.

Investigations indicate that best results in the preliminary set-up are attainable by working at the extreme top of the peaks, thereby avoiding confusion due to the two lines corresponding to the two sides of the pulses. This is due to the fact that at high mirror speeds (giving high resolution) these lines may be some distance apart (in the absence of extremely sharp transmitted pulses and a very carefully designed receiver having negligible time constants). Developments are hence in progress to attain these desirable features in transmission and reception. These double lines are most confusing in the presence of multiple layers. Under such conditions it is difficult to recognize whether specific lines correspond to upward or downward motions of the light beam from the base line of the peaks. The tops of the peaks are readily maintained at a fixed height by arranging the resistance-coupled amplifier circuit so that the incoming signal reduces rather than increases the current through the element. It is readily possible with a high gain set such as employed in the experiments described, to reduce this current to practically zero when the incoming pulse has a moderate amplitude. This results in a fixed position of the top of the pulses which corresponds to the zero

TABLE 6.—*Data*

SURFACE SI

Basic paper-machine run No.	Surface-sizing run No.	Beating interval	Freeness of stock		Rosin size, amount rosin based on dry fiber	Alum, amount based on dry fiber	Acidity of stock at head box	Sizing solution		Sizing preservative		Temperature of sizing bath	Acidity of sizing bath	Aging test		Weight, 500 sheets 25 by 40 inches	Bursting strength	Ratio of bursting strength to weight	Thickness	Folding endurance			Folding endurance in percent of initial			Te
			After beating	At head box				Kind	Amount of solution	Kind	Amount based on size in bath			Temperature	Duration					Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	M ch di ti
		Hours			*Per cent*	*Per cent*	*pH*		*Per cent*		*Per cent*	*°F.*	*pH.*	*°C.*	*Hours*	*Pounds*	*Points* [1]	*Per cent*	*Inch*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	
785		7	146	78	0	0										57.2	45.0	79	0.0040	3,400	4,380	3,890				
														100	72	59.9	41.8	70		3,160	4,280	3,720	93	98	99	
785	169							Glue	4	None		130	6.0			59.1	62.1	105	.0037	3,830	4,960	4,400				1
														100	72	59.7	61.2	103		3,830	4,800	4,320	100	97	99	1
796		7	163	97	0.5	0.8	5.5									56.1	42.5	76	.0041	2,980	3,980	3,480				
														100	72	55.6	41.7	75		2,390	3,210	2,800	80	81	81	
796	170							Glue	4	None		130	6.0			57.9	53.1	92	.0037	3,510	4,320	3,920				1
														100	72	57.3	53.3	93		3,020	4,010	3,520	86	93	90	1
787		7	143	85	1.0	1.0	5.0									53.3	37.2	70	.0038	2,810	2,470	2,640				
														100	72	53.6	36.1	67		2,210	2,090	2,150	79	85	82	
787	171							Glue	4	None		130	6.0			54.6	44.4	81	.0036	3,050	3,190	3,120				
														100	72	53.9	46.7	87		2,590	2,870	2,730	86	90	88	
787	172							Glue	4	Formal-dehyde	0.25	130	5.7			57.0	45.9	80	.0037	2,910	3,490	3,200				
														100	72	57.2	46.9	82		2,470	3,110	2,790	85	89	87	
785		7	146	78	0	0										56.1	44.6	79	.0041	4,160	4,540	4,350				
														100	72	55.9	40.4	72		4,320	4,650	4,490	104	102	103	
788	173							Glue	4	Alum	7	130	4.2			58.3	62.9	108	.0034	4,100	4,410	4,260				
														100	72	57.5	64.5	112		3,830	4,190	4,010	93	95	94	
796		7	163	97	.5	.8	5.5									55.6	40.9	74	.0041	3,550	3,560	3,560				
														100	72	55.8	43.9	79		3,050	2,770	2,910	86	78	82	
796	174							Glue	4	Alum	7	130	4.2			57.2	53.2	91	.0033	3,970	3,330	3,650				
														100	72	57.0	51.3	90		3,180	3,070	3,130	80	92	86	
787		7	143	85	1.0	1.0	5.0									53.9	37.2	69	.0037	2,570	2,370	2,470				
														100	72	54.1	38.0	70		2,100	2,120	2,110	82	89	86	
787	175							Glue	4	Alum	7	130	4.2			54.3	44.9	83	.3332	2,460	3,080	2,770				
														100	72	55.2	45.2	82		2,100	2,510	2,310	85	81	83	

SURFACE SIZED WITH STARCH PR

785		7	146	78	0	0										56.0	41.8	75	0.0036	4,080	4,530	4,310				
														100	72	55.7	44.6	80		3,690	3,760	3,730	90	83	87	
785	176							Starch	4	None		130	7.3			58.2	64.0	110	.0034	4,670	4,110	4,390				
														100	72	58.2	60.8	105		4,300	4,530	4,420	92	110	101	
796		7	163	97	0.5	0.8	5.5									54.4	41.2	76	.0036	3,870	2,990	3,430				
														100	72	54.8	40.5	74		3,380	2,970	3,180	87	99	93	
796	177							Starch	4	None		130	7.3			57.5	52.2	91	.0035	4,310	3,620	3,970				
														100	72	57.1	49.3	86		4,000	2,720	3,360	93	75	84	
787		7	143	85	1.0	1.0	5.0									56.0	36.8	66	.0035	3,240	2,620	2,930				
														100	72	55.5	38.0	68		2,560	1,970	2,270	79	75	77	
787	178							Starch	4	None		130	7.3			56.2	43.9	78	.0033	3,120	2,640	2,880				
														100	72	56.0	44.8	80		2,700	2,600	2,650	86	98	92	
785		7	146	78	0	0										55.4	41.4	75	.0036	4,110	4,500	4,310				
														100	72	55.5	42.1	76		3,850	4,300	4,080	94	96	95	
785	179							Starch	4	Alum	2	130	5.4			59.3	62.8	106	.0035	4,740	5,210	4,980				
														100	72	57.1	60.0	105		4,350	4,640	4,500	92	89	91	
796		7	163	97	.5	.8	5.5									55.5	42.6	77	.0036	3,720	2,810	3,270				
														100	72	55.6	43.7	79		3,060	2,730	2,900	82	97	90	
796	180							Starch	4	Alum	2	130	5.4			57.4	52.1	91	.0034	3,940	3,320	3,630				
														100	72	57.1	52.1	91		3,870	3,150	3,510	98	95	97	
787		7	143	85	1.0	1.0	5.0									56.7	36.9	65	.0036	2,760	2,440	2,600				
														100	72	56.3	39.8	71		2,000	2,150	2,080	72	88	80	
787	181							Starch	4	Alum	2	130	5.4			57.9	44.3	77	.0035	2,800	3,510	3,160				
														100	72	58.6	45.0	77		2,960	2,960	2,960	106	84	95	

SURFACE SIZED WITH STARCH

785		7	146	78	0	0										59.2	45.4	77	0.0039	4,180	4,560	4,370				
														100	72	57.9	44.4	77		4,400	5,340	4,870	105	117	111	
785	188							Starch	4	None		130	7.2			60.6	60.3	100	.0036	4,350	5,410	4,880				
														100	72	57.8	61.3	106		4,410	5,650	5,030	101	104	103	
785	185							Starch	4	Alum	2	130	4.6			56.8	57.4	101	.0035	4,130	5,660	4,900				
														100	72	56.3	60.5	107		4,210	4,640	4,430	102	82	92	
796		7	163	97	0.5	0.8	5.5									54.7	41.8	76	.0035	4,450	3,170	3,810				
														100	72	52.2	43.4	83		4,020	2,350	3,190	90	74	82	
796	186							Starch	4	Alum	2	130	4.6			56.4	48.3	86	.0033	4,390	3,320	3,860				
														100	72	53.6	50.9	95		4,100	3,080	3,590	93	93	93	
787		7	143	85	1.0	1.0	5.0									56.9	38.4	67	.0036	3,440	2,810	3,130				
														100	72	54.8	40.2	73		2,520	3,000	2,760	73	107	90	
787	189							Starch	4	None		130	7.2			55.6	45.5	82	.0033	3,190	3,080	3,140				
														100	72	54.7	44.8	82		2,470	2,540	2,510	77	82	80	
787	187							Starch	4	Alum	2	130	4.6			59.3	45.4	77	.0035	2,860	3,470	3,170				
														100	72	56.0	42.9	77		2,420	3,240	2,830	85	93	89	

[1] Approximately pounds per square inch.

TABLE 6.—*Data on surface-sized papers*

SURFACE SIZED WITH GLUE

Bursting strength	Ratio of bursting strength to weight	Thickness	Physical tests: Folding endurance			Folding endurance in per cent of initial			Tensile breaking strength			Elongation at rupture			Tearing streng	
			Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	Across machine direction	Average	Machine direction	Across machine direction
Points [1]	*Per cent*	*Inch*	*Double folds*	*Double folds*	*Double folds*	*Per cent*	*Per cent*	*Per cent*	*kg*	*kg*	*kg*	*Per cent*	*Per cent*	*Per cent*	*g*	*g*
45.0	79	0.0040	3,400	4,380	3,890				9.32	6.14	7.73	2.65	7.05	4.85	103.2	107.6
41.8	70		3,160	4,280	3,720	93	98	99	9.02	6.07	7.55	2.80	6.60	4.70	86.0	101.2
62.1	105	.0037	3,830	4,960	4,400				11.26	8.07	9.67	3.65	8.20	5.95	62.6	72.4
61.2	103		3,830	4,800	4,320	100	97	99	11.35	8.11	9.73	3.80	9.00	6.40	69.0	76.2
42.5	76	.0041	2,980	3,980	3,480				8.89	5.68	7.29	2.85	7.30	5.10	94.8	102.4
41.7	75		2,390	3,210	2,800	80	81	81	9.08	5.71	7.40	2.60	7.00	4.80	82.0	87.6
53.1	92	.0037	3,510	4,320	3,920				10.38	7.11	8.75	3.50	8.45	6.00	85.0	90.2
53.3	93		3,020	4,010	3,520	86	93	90	10.91	7.02	8.97	3.60	8.20	5.90	71.8	75.8
37.2	70	.0038	2,810	2,470	2,640				8.28	4.97	6.63	2.65	7.30	5.00	92.0	97.6
36.1	67		2,210	2,090	2,150	79	85	82	8.34	5.05	6.70	2.80	7.80	5.30	84.8	86.8
44.4	81	.0036	3,050	3,190	3,120				8.98	5.81	7.40	3.35	7.80	5.60	73.8	77.8
46.7	87		2,590	2,870	2,730	85	90	88	8.94	5.87	7.41	3.20	8.35	5.80	74.4	77.8
45.9	80	.0037	2,910	3,480	3,200				9.46	6.05	7.76	3.10	8.35	5.75	81.6	86.4
46.9	82		2,470	3,110	2,790	85	89	87	9.59	5.92	7.76	3.35	7.95	5.65	69.6	77.6
44.6	79	.0041	4,160	4,540	4,350				9.49	5.79	7.64	2.65	7.55	5.10	94.8	95.2
40.4	72		4,320	4,650	4,490	104	102	103	9.27	5.65	7.46	2.60	7.60	5.10	84.8	92.6
62.9	108	.0034	4,100	4,410	4,260				11.91	8.23	10.07	3.80	8.65	6.25	72.0	76.2
64.5	112		3,830	4,190	4,010	93	95	94	11.70	7.98	9.84	3.90	8.95	6.45	64.6	70.8
40.9	74	.0041	3,550	3,560	3,560				8.61	5.46	7.04	2.80	7.90	5.35	95.6	95.6
43.9	79		3,050	2,770	2,910	86	78	82	9.42	5.42	7.42	2.70	7.85	5.30	82.0	90.8
52.2	91	.0033	3,970	3,330	3,650				10.76	6.46	8.61	3.50	8.70	6.10	75.1	80.0
51.3	90		3,180	3,070	3,130	80	92	86	10.13	6.30	8.22	3.45	8.70	6.10	72.0	79.0
37.2	69	.0037	2,570	2,370	2,470				7.74	5.26	6.50	2.60	8.05	5.35	91.2	97.2
38.0	70		2,100	2,120	2,110	82	89	86	8.14	5.22	6.68	2.65	7.80	5.25	83.6	76.8
44.9	83	.3332	2,460	3,080	2,770				9.16	5.90	7.53	3.25	9.00	6.15	79.0	80.8
45.2	82		2,100	2,510	2,310	85	81	83	9.32	5.86	7.59	3.05	8.15	5.60	71.0	75.8
SURFACE SIZED WITH STARCH PREPARED BY A PROCESS OF ACID HYDROLYSIS																
41.8	75	0.0036	4,080	4,530	4,310				9.26	5.57	7.42	2.75	7.70	5.25	93.2	103.2
44.6	80		3,690	3,760	3,730	90	83	87	9.23	5.72	7.48	2.55	7.55	5.05	88.4	88.0
64.0	110	.0034	4,670	4,110	4,390				11.49	7.88	9.69	3.90	9.50	6.70	72.2	78.8
60.8	105		4,300	4,530	4,420	92	110	101	11.48	7.90	9.69	3.90	9.55	6.75	69.0	73.6
41.2	76	.0036	3,870	2,990	3,430				8.80	5.01	6.91	2.80	7.65	5.15	101.6	98.8
40.5	74		3,380	2,970	3,180	87	99	93	8.88	5.01	6.95	2.80	8.10	5.45	90.4	90.0
52.2	91	.0035	4,310	3,620	3,970				9.68	6.04	7.86	3.25	8.75	6.00	84.2	85.4
49.3	86		4,000	2,720	3,360	93	75	84	10.14	6.18	8.16	3.40	8.85	6.15	75.8	77.8
36.8	66	.0035	3,240	2,620	2,930				8.67	5.18	6.93	3.05	7.85	5.45	94.4	105.2
38.0	68		2,560	1,970	2,270	79	75	77	8.61	5.34	6.98	2.80	8.00	5.40	88.0	88.4
43.9	78	.0033	3,120	2,640	2,880				8.85	5.76	7.31	3.40	8.80	6.10	90.2	94.2
44.8	80		2,700	2,600	2,650	86	98	92	9.01	5.73	7.37	3.20	8.55	5.90	79.0	80.8
41.4	75	.0036	4,110	4,500	4,310				8.92	5.62	7.27	2.80	7.70	5.25	91.6	100.0
42.1	76		3,850	4,300	4,080	94	96	95	9.02	5.30	7.16	3.10	7.35	5.25	88.0	92.4
62.8	106	.0035	4,740	5,210	4,980				11.19	7.60	9.40	3.85	9.05	6.45	73.2	77.2
60.0	105		4,350	4,640	4,500	92	89	91	10.63	7.28	8.96	3.85	9.05	6.45	65.2	72.8
42.6	77	.0036	3,720	2,810	3,270				8.79	5.29	7.04	2.95	7.65	5.30	92.8	109.6
43.7	79		3,060	2,730	2,900	82	97	90	8.97	5.49	7.23	2.80	7.50	5.15	86.8	96.4
52.1	91	.0034	3,940	3,320	3,630				9.51	6.45	7.98	3.35	8.85	6.10	83.0	88.6
52.1	91		3,870	3,150	3,510	98	95	97	10.13	6.05	8.09	3.45	8.50	6.00	76.6	77.4
36.9	65	.0036	2,760	2,440	2,600				8.95	5.42	7.19	2.90	8.05	5.50	99.6	104.4
39.8	71		2,000	2,150	2,080	72	88	80	8.91	5.29	7.10	2.80	7.60	5.20	85.6	89.6
44.3	77	.0035	2,800	3,510	3,160				9.63	5.75	7.69	3.40	8.40	5.90	93.2	98.0
45.0	77		2,960	2,960	2,960	106	84	95	9.47	5.71	7.59	3.20	7.95	5.60	79.6	84.6
SURFACE SIZED WITH STARCH PREPARED BY A PROCESS OF OXIDATION																
45.4	77	0.0039	4,180	4,560	4,370				9.19	5.83	7.51	2.60	8.40	5.50	97.6	100.4
44.4	77		4,400	5,340	4,870	105	117	111	8.76	5.70	7.23	2.75	9.25	6.00	93.6	100.4
60.3	100	.0036	4,350	5,410	4,880				10.40	7.61	9.01	3.35	10.05	6.70	75.6	74.8
61.3	106		4,410	5,650	5,030	101	104	103	10.48	7.28	8.88	3.65	9.70	6.70	74.4	68.0
57.4	101	.0035	4,130	5,660	4,900				10.69	7.77	9.23	3.45	10.10	6.80	82.4	71.6
60.5	107		4,210	4,640	4,430	102	82	92	10.38	7.04	8.71	3.95	10.35	7.15	65.6	73.6
41.8	76	.0035	4,450	3,170	3,810				9.03	4.86	6.95	2.55	7.95	5.25	97.2	90.4
43.4	83		4,020	2,350	3,190	90	74	82	8.76	4.90	6.83	2.95	8.80	5.90	86.8	87.2
48.3	86	.0033	4,390	3,320	3,860				9.89	5.95	7.92	3.15	9.95	6.55	72.8	70.4
50.9	95		4,100	3,080	3,590	93	93	93	9.52	5.58	7.55	3.50	9.75	6.65	68.0	72.8
38.4	67	.0036	3,440	2,810	3,130				8.76	5.25	7.01	2.50	7.90	5.20	88.4	94.4
40.2	73		2,520	3,000	2,760	73	107	90	7.87	5.15	6.51	2.75	8.50	5.65	91.2	86.0
45.5	82	.0033	3,190	3,080	3,140				8.92	5.46	7.19	3.45	8.95	6.20	70.6	75.2
44.8	82		2,470	2,540	2,510	77	82	80	8.71	5.30	7.01	3.25	9.55	6.40	70.0	72.0
45.4	77	.0035	2,860	3,470	3,170				9.05	5.39	7.22	2.85	8.65	5.75	86.4	88.4
42.9	77		2,420	3,240	2,830	85	93	89	8.79	5.46	7.13	3.10	8.25	5.70	74.8	76.4

[1] pounds per square inch.

Tearing strength		Tearing strength in per cent of initial			Opacity	Sizing quality			Chemical tests												
									Ash	Sizing materials present		Acidity					Alpha cellulose content	Alpha cellulose content, corrected for sizing materials present	Decrease in alpha cellulose content on heating	Copper number	Increase in copper number on heating
												By Kohler-Hall method			Fiber suspension	Fiber extract[1]					
Across machine direction	Average	Machine direction	Across machine direction	Average		Indicator (21° C.)	Curl (21° C.)	Wet rub		Rosin	Glue	Total	External	Internal							
g	*g*	*Per cent*	*Per cent*	*Per cent*		*Seconds*	*Seconds*	*Double rubs*	*Per cent*	*Per cent*	*Per cent*	*Per cent*[2]	*Per cent*[2]	*Per cent*[2]	*Per cent*[2]	*pH*	*Per cent*	*Per cent*	*Per cent*		
107.6	105.4				78.8				0.20	0.1		0.006		0.006	0.008	6.6	90.2	90.3		0.67	
101.2	93.6	83	94	89													89.8		0.5	.78	0.11
72.4	67.5				77.2	2.5	2.4	28	.23	.1	2.52	0.18	0.006	.012	.019	6.4	87.4	89.7		.87	
76.2	72.6	110	105	108													87.5		.1	.87	.00
102.4	98.6				79.0	12.1	12.8		.31	.5		.031		.031	.083	4.9	89.0	89.5		.80	
87.6	84.8	87	86	87													87.9		1.1	1.01	.21
90.2	87.6				77.7	17.6	20.8	38	.34	.4	1.31	.034	.007	.027	.087	5.0	87.3	88.8		.88	
75.8	73.8	84	84	84													86.7		.7	1.06	.18
97.6	94.8				78.8	21.8	22.0		.34	.9		.048		.048	.115	4.8	88.0	88.8		.94	
86.8	85.8	92	89	91													85.7		2.6	1.25	.31
77.8	75.8				76.8	20.2	19.5	36	.37	.9	.96	.049	.010	.039	.115	4.8	87.0	88.7		.88	
77.8	76.1	101	100	101													86.3		.8	1.06	.18
86.4	84.0				77.6	22.7	19.3	41	.35	.9	.94	.045	.009	.036	.116	4.6	86.6	88.2		.92	
77.6	73.6	85	90	88													85.5		1.3	1.28	.36
95.2	95.0				78.8				.20	.1		.006		.006	.008	6.6	90.2	90.3		.67	
92.6	88.7	89	97	93													89.8		.5	.78	.11
76.2	74.1				75.3	7.4	10.5	37	.30	.1	1.97	.032	.010	.022	.059	5.2	87.8	89.6		.81	
70.8	67.7	90	93	92													87.6		.2	.97	.16
95.6	95.6				79.0	12.1	12.8		.31	.5		.031		.031	.083	4.9	89.0	89.5		.80	
90.8	86.4	86	95	91													87.9		1.1	1.01	.21
80.0	77.6				78.0	18.9	17.3	44	.32	.5	1.00	.046	.012	.034	.116	4.6	87.8	89.1		.84	
79.0	75.5	96	99	98													87.3		.5	1.01	.17
97.2	94.2				78.8	21.8	22.0		.34	.9		.048		.048	.115	4.8	88.0	88.8		.94	
76.8	80.2	92	79	86													85.7		2.6	1.25	.31
80.8	79.9				77.4	21.5	20.6	44	.33	.9	.81	.058	.014	.044	.129	4.4	87.2	88.7		.97	
75.8	73.4	90	94	92													86.7		.6	1.12	.15
SIS																					
103.2	98.2				78.8				0.20	0.1		0.006		0.006	0.008	6.6	90.2	90.3		0.67	
88.0	88.2	95	85	90													89.8		0.5	.78	0.11
78.8	75.5				75.6	2.7	3.0	15	.27	.1	1.98	.005	0.001	.004	.001	6.6	89.6	91.5		.67	
73.6	71.3	96	93	95													89.4		.2	.76	.09
98.8	100.2				79.0	12.1	12.8		.31	.5		.031		.031	.083	4.9	89.0	89.5		.80	
90.0	90.2	89	91	90													87.9		1.1	1.01	.21
85.4	84.8				78.4	19.0	19.2	27	.30	.4	.93	.030	.004	.026	.062	5.3	89.2	90.5		.75	
77.8	76.8	90	91	91													88.3		1.0	.96	.21
105.2	99.8				78.8	21.8	22.0		.34	.9		.048		.048	.115	4.8	88.0	88.8		.94	
88.4	88.2	93	84	89													85.7		2.6	1.25	.31
94.2	92.2				78.6	14.5	18.4	32	.38	.8	.73	.047	.006	.041	.099	4.9	89.2	90.5		.83	
80.8	79.9	88	86	87													87.9		1.5	1.11	.28
100.0	95.8				78.8				.20	.1		.006		.006	.008	6.6	90.2	90.3		.67	
92.4	90.2	96	92	94													89.8		.5	.78	.11
77.2	75.2				74.3	2.6	2.7	16	.28	.1	1.98	.007	.002	.005	.010	6.7	89.4	91.3		.67	
72.8	69.0	89	94	92													88.9		.6	.82	.15
109.6	101.2				79.0	12.1	12.8		.31	.5		.031		.031	.083	4.9	89.0	89.5		.80	
96.4	91.6	94	88	91													87.9		1.1	1.01	.21
88.6	85.8				78.5	21.2	20.1	26	.33	.4	1.08	.030	.005	.025	.078	5.2	89.1	90.5		.79	
77.4	77.0	92	87	90													88.6		.7	.94	.15
104.4	102.0				78.8	21.8	22.0		.34	.9		.048		.048	.115	4.8	88.0	88.8		.94	
89.6	87.6	86	86	86													85.7		2.6	1.25	.31
98.0	95.6				78.4	18.2	20.4	38	.38	.9	.76	.049	.008	.041	.119	4.8	88.8	90.3		.90	
84.6	82.1	85	86	86													87.6		1.3	1.19	.29
100.4	99.0				80.7				0.19	0.1					0.008	6.6	90.2	90.3		0.67	
100.4	97.0	96	100	98													89.8		0.5	.78	0.11
74.8	75.2				76.8	2.4	2.6	15	.17	.2	2.14				.006	6.7	88.3	90.4		.69	
68.0	71.2	98	91	95													88.1		.2	.78	.09
71.6	77.0				77.9	3.6	3.7	21	.19	.2	1.96				.020	6.4	87.9	89.9		.62	
73.6	69.6	80	103	92													87.7		.2	.85	.23
90.4	93.8				80.1	12.1	12.8		.30	.5					.083	4.9	89.0	89.5		.80	
87.2	87.0	89	96	93													87.9		1.1	1.01	.21
70.4	71.6				76.4	21.2	19.3	29	.27	.7	.92				.074	5.0	88.1	89.5		.73	
72.8	70.4	93	103	98													87.5		.7	.96	.23
94.4	91.4				80.0	19.7	19.6		.33	.9					.115	4.8	88.0	88.8		.94	
86.0	88.6	103	91	97													85.7		2.6	1.25	.31
75.2	72.9				77.3	20.5	24.4	37	.31	1.2	.61				.085	4.8	87.8	89.4		.62	
72.0	71.0	99	96	98													86.9		1.0	.85	.23
88.4	87.4				80.3	21.1	21.8	37	.31	1.3	.72				.110	4.7	87.9	89.7		.99	
76.4	75.6	87	87	87													86.7		1.4	1.25	.26

[1] Acidity calculated as per cent SO_4.

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current position of the light beam. This position has the advantage of being practically unaffected by changes in the operating plate current of the last amplifier tube due to voltage fluctuations, etc.

V. CONCLUSION

Aside from developments for improving the reliabilty of the recording system so as to insure the continuity of records, it appears probable that problems arising in the interpretation of these records are likely to be of paramount importance. Thus, the complex records obtained in the presence of "split peaks," multiple reflections, and other intricate phenomena, greatly complicate the work of interpretation of the records. Reinforced and interpreted by supplementary records taken by the oscillographic methods previously employed, however, continuous records of this kind represent a distinct addition to the methods heretofore available for the study of Kennelly-Heaviside layer phenomena.

WASHINGTON, August 21, 1931.

THE RELATIVE SPECTRAL ENERGY DISTRIBUTION AND CORRELATED COLOR TEMPERATURE OF THE N. P. L. WHITE-LIGHT STANDARD

By Raymond Davis and K. S. Gibson

ABSTRACT

The spectral characteristics of the two Guild-Young filters have been deduced from their specifications. The first of these filters, in conjunction with a source having the relative spectral energy distribution given by Planck's formula for a temperature of 2,360° K., is used to calibrate a gas-filled lamp. This lamp is used in turn with the second filter to produce the N. P. L. standard white light.

Our computations indicate that the chromaticity of the first source-and-filter combination approximates closely that of a Planckian radiator at 2,931° K. Using as a source the relative spectral energy distribution corresponding to 2,931° K. in combination with the second filter we have obtained the spectral energy distribution and the chromaticity of the N. P. L. white-light standard. This latter turns out to be approximately that of a Planckian radiator at 4,831° K. Comparison is made with the Davis-Gibson source-filter combination for obtaining a color temperature of 4,800° K.

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I. INTRODUCTION

About five years ago Guild [1] described two filters devised by his colleague, Dr. A. F. A. Young, to be used in establishing a working standard of "white light" for colorimetric purposes. The first of these filters was designed to convert the light from a lamp operating at a color temperature of 2,360° K. to a chromaticity approximating that of 3,000° K., so that a second lamp might be calibrated at this latter chromaticity by the 2,360° K. source-and-filter combination using standard photometric apparatus. The second filter was to be used with this second lamp, calibrated as described, to produce the N. P. L. white light, having a chromaticity approximating that of 5,000° K. It was emphasized in Guild's paper that the values given were "provisional" only, and that full details as to the energy distribution would be forthcoming later.

Recently Wright [2] has used these filters in setting up a stimulus which he used in a redetermination of the "trichromatic coefficients" for 10 observers. In the appendix to Wright's paper the following statement appears: "During the discussion of the paper it was pointed out by Mr. Guild that the standard white specified by the National

[1] J. Guild, Trans. Opt. Soc. vol. 27; pp. 122–124; 1925–26.
[2] W. D. Wright, A Redetermination of the Trichromatic Coefficients of the Spectral Colors, Trans. Opt. Soc., vol. 30, pp. 141–164; 1928–29.

Physical Laboratory did not, as stated, provide a source with a color temperature of 5,000° K., but one with a color temperature more nearly 4,800° K. To avoid confusion, the complete specification is given in this appendix." There follows the specification [3] of the two Guild-Young filters, one used to calibrate a gas-filled lamp, which is in turn used with the second filter to produce the standard white. In this connection it is remarked, "In this way the gas-filled lamp is rated to a definite color temperature, although the actual value of this temperature does not appear in the specification. * * * The color temperature actually obtained in this way is at present believed to be very close to 2,900° K. The energy distribution (of the standard white) departs appreciably from that of a black body but the integral color matches that of a black body at a temperature of approximately 4,800° K."

Apparently the spectral energy distribution of the N. P. L. standard white was not published until recently, although the desirability of such publication is quite evident.[4] Because of this lack of spectrophotometric data, Dr. D. B. Judd, of the colorimetry section, requested the authors, in 1930, to determine the spectral energy distribution of the N. P. L. standard white light, as he desired to make an analytical study of Wright's [5] new data.

II. METHOD USED TO DERIVE THE VALUES

We have derived the spectral energy distribution of the N. P. L. standard white from the specification of the two liquid filters. Each filter consists of two compartments; the absorbing materials in one compartment are copper sulphate and cobalt sulphate, for which standard data were already available;[6] that in the other is ammoniacal copper sulphate. The spectral transmittancies [7] of the specified solutions of ammoniacal copper sulphate were determined by methods previously described by the authors.[8] They are given in Table 1. From these component data the spectral transmissions of the filters were computed; these values for the white-light filter are given in Table 1.

The relative spectral distribution of energy was then computed for the lamp-rating filter combined with a Planckian radiator at 2,360° K., as specified by Guild. From this distribution the trilinear coordinates were computed on the basis of mean sun [9] at the center of the Maxwell triangle. As these r, g, and b values did not agree

[3] As noted in B. S. Misc. Pub. No. 114, p. 9, footnote 4, the specification of the white-light filter as given by Wright is slightly different from that originally given by Guild. In the present computations the revised specification was used. This revised specification is also given in a recent paper by Guild, reference in footnote 16.

[4] See discussion of Wright's paper (Trans. Opt. Soc., vol. 30, p. 161, 1928–29) by Prof. L. C. Martin.

[5] See footnote 2.

[6] Raymond Davis and K. S. Gibson, Filters for the Reproduction of Sunlight and Daylight and for the Determination of Color Temperature, Misc. Pub. 114, Tables 5 and 6, p. 42. The values for the 2-compartment cell filled with water, Table 7, p. 43, were likewise assumed to be valid for the present computations.

[7] For the spectrophotometric terminology used here, see B. S. Misc. Pub. No. 114, pp. 38–39.

[8] However, the measurements on which the present data are based are far less extensive than t hose carried out in the determination of the characteristics of the pyridine-mannite solution of copper sulphate specified in Table 4, p. 41, of B. S. Misc. Pub. No. 114. No photoelectric or thermoelectric measurements were made. Only one solution of each kind was examined, visual measurements being made on two thicknesses of each of the two solutions at each of 18 wave lengths distributed between 404.7 and 710 mμ. The temperature of the solutions was 25° C. The authors are indebted to Mabel E. Brown for these measurements. In reducing the data the experimental values thus obtained were compared with data previously obtained on solutions of different ammonia content. Such comparison assisted considerably in the adoption of values at every 10 mμ below 500 mμ, but contributed much less at wave lengths above 500 mμ.

[9] See B. S. Misc. Pub. No. 114, Table 1, fig. 12.

exactly with those for the Planckian radiator[10] at any temperature, it was necessary to deduce the nearest color temperature resulting from this combination. This was done by Davis's method for determining "correlated color temperature," described in a recent publication[11] and previously used by the authors in connection with certain of their filters.[12]

After the correlated color temperature had thus been obtained with the 2,360° K. source and the lamp-rating filter, similar computations were made for a Planckian radiator at this temperature in combination with the N. P. L. white-light filter.

TABLE 1.—*Spectrophotometric data for the N. P. L. standard white as determined by the present authors*

Wave length in mμ	Spectral transmittancy of n grams of $CuSO_4.5H_2O$ and 100 n cc 28 per cent ammonia per 1,000 cc of aqueous solution.		Spectral transmission of N. P. L. white-light filter	Spectral energy distribution of N. P. L. standard white	Wave length in mμ	Spectral transmittancy of n grams of $CuSO_4.5H_2O$ and 100 n cc 28 per cent ammonia per 1,000 cc of aqueous solution		Spectral transmission of N. P. L. white-light filter	Spectral energy distribution of N. P. L. standard white
	n=1.41	n=2.30				n=1.41	n=2.30		
380	0.991	0.955	0.822	33.83	560	0.574	0.407	0.300	111.84
390	.993	.968	.832	41.88	570	.542	.368	.285	113.34
400	.993	.975	.830	50.33	580	.515	.336	.265	112.12
410	.993	.979	.823	59.49	590	.494	.310	.243	108.78
420	.993	.982	.811	69.00	600	.479	.290	.222	104.82
430	.991	.979	.780	77.42	610	.470	.275	.204	101.63
440	.986	.973	.730	83.63	620	.467	.267	.191	99.60
450	.979	.962	.664	87.10	630	.469	.265	.180	98.19
460	.966	.944	.599	89.10	640	.475	.269	.171	97.43
470	.946	.916	.547	91.74	650	.485	.277	.163	96.81
480	.923	.879	.502	94.08	660	.499	.288	.156	96.43
490	.891	.832	.456	94.86	670	.514	.302	.1487	94.97
500	.849	.774	.402	92.36	680	.531	.317	.1412	93.24
510	.802	.713	.356	89.93	690	.548	.333	.1323	90.20
520	.752	.649	.330	90.73	700	.566	.349	.1239	86.93
530	.703	.583	.320	95.50	710	.585	.366	.1160	83.69
540	.655	.518	.316	102.06	720	.603	.384	.1078	79.77
550	.612	.458	.311	108.09					

III. RESULTS OBTAINED

The spectral distribution of energy of the N. P. L. standard white as thus derived is given in Table 1. The colorimetric data for the two lamp-and-filter combinations—viz, the temperature of the Planckian radiator taken as the source in each case, and the trilinear coordinates, the correlated color temperature, the color departure,[11] and the conjunctive wave length [11] for the combinations—are given in Table 2. The color departure and the conjunctive wave length together indicate the nature of the difference between the colors represented by the source-and-filter combinations and the Planckian radiator at the respective correlated temperatures. The unit used in specifying the color departure is equal to about one-fifth of a satron.[13]

[10] Values of r, g, and b for the Planckian radiator over the temperature range from 1,600° to 20,000° K. are given in Table 11 of B. S. Misc. Pub. No. 114. They are based on computations with mean sun at the center of the Maxwell triangle.

[11] Raymond Davis, A Correlated Color Temperature for Illuminants, B. S. Jour. Research, vol. 7, p. 659; 1931.

[12] B. S. Misc. Pub. No. 114, Tables 13 to 15.

[13] See B. S. Misc. Pub. No. 114, p. 121, for definition of satron.

Recently Guild has published the relative spectral energy distribution of the N. P. L. standard white.[14] The values disagree somewhat from ours. The two sets of relative energy values, along with those for a Planckian radiator at 4,800° K., are shown in Figure 1. The colorimetric characteristics corresponding to the distribution given by Guild are presented in Table 2. It may be noted that the correlated color temperature obtained from Guild's values is 4,816° K. as compared with 4,831° K. obtained from our data. Judd's analysis indicates [15] that the difference in energy distribution and color obtained in these two determinations has no important bearing on the significance of Wright's data. Part of the discrepancy lies, of course, in the source used with the filter. We used the relative energy distribution of a Planckian radiator at 2,931° K., whereas Guild used an energy distribution corresponding to 2,900° K.

TABLE 2.—*Colorimetric characteristics of the Guild-Young lamp-and-filter combinations*

Designation of filter in combination with specified light source	Source of energy data	Source (Planckian radiator) at—	Trilinear coordinates			Correlated color temperature	Color departure $\frac{+}{\delta}$	Conjunctive wave length λ_f
			r	g	b			
								$m\mu$
Lamp-rating filter	Authors	2,360° K	0.4640_8	0.3618_8	0.1740_8	2,931° K	0.9	57
White-light filter	do	2,931°	$.3442_7$	$.3301_2$	$.3256_1$	4,831°	2.2	56
Do	Guild	(2,900°)	$.3463_1$	$.3323_4$	$.3213_3$	4,816°	3.9	56

Guild has published [16] values of spectral "transmission coefficient" for the white-light filter over a wave-length range from 400 to 780 mμ. His values, however, appear to be what we would define as transmittance, or transmission corrected for reflection losses. His values were multiplied by 0.9 (in order to introduce approximately these reflection losses) and then compared with ours, and it was found that from 400 to 690 mμ, inclusive, the algebraic sum of the discrepancies is practically zero; and, except at 690 mμ, the maximum deviation from the mean is not greater than ± 1.5 per cent of the mean value. The discrepancy becomes considerable at 720 mμ, but this has little effect on the colorimetric use of the filter.

IV. COMPARISON WITH DAVIS-GIBSON SOURCE-FILTER COMBINATION

It was of interest to the authors to compare the energy distribution obtained for the N. P. L. standard white with that resulting from one of their filters—that designed to convert the chromaticity of a Planckian radiator at 2,848° K. to that for 4,800° K. The energy distribution for this particular filter had not previously been computed, although it could be closely estimated from the distributions

[14] J. Guild, The Colorimetric Properties of the Spectrum, Phil. Trans. Roy. Soc. London, vol. 230, p. 179, June, 1931.
[15] D. B. Judd, Comparison of Wright's data on Equivalent Color Stimuli with the O. S. A. data, J. Opt. Soc. Am., 21; 1931.
[16] J. Guild, On the Fixed Points o a Colorimetric System (advanced proof), Trans. Opt. Soc., 32, p. 21, 1930-31. In this paper are also given Guild's revised specifications for the white-light filter.

given in Charts 22 to 25 of B. S. Misc. Pub. No. 114. The concentrations of the components of this filter are, however, given in Table 12 (p. 61) of that publication.

The energy distribution derived from these concentrations (with source at 2,848° K., as with the other filters of this series) is shown in Figure 1, and also in the accompanying chart (fig. 2), which gives the chemical and spectrophotometric specification for this filter. The trilinear coordinates derived from this energy distribution do not differ from those for a Planckian radiator at 4,800° K. by more than 0.0001. This is an excellent check on the reliability of the concentrations of the components given at the various intermediate temperatures in

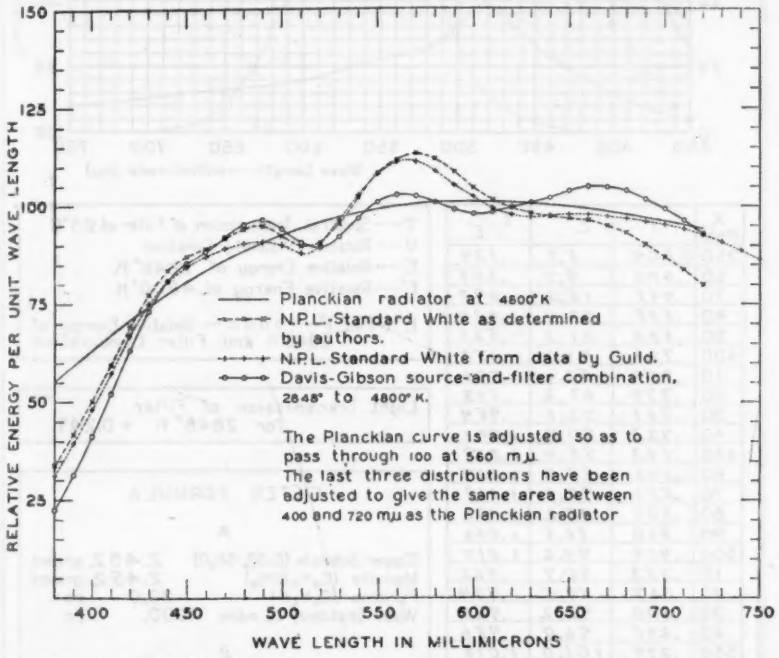
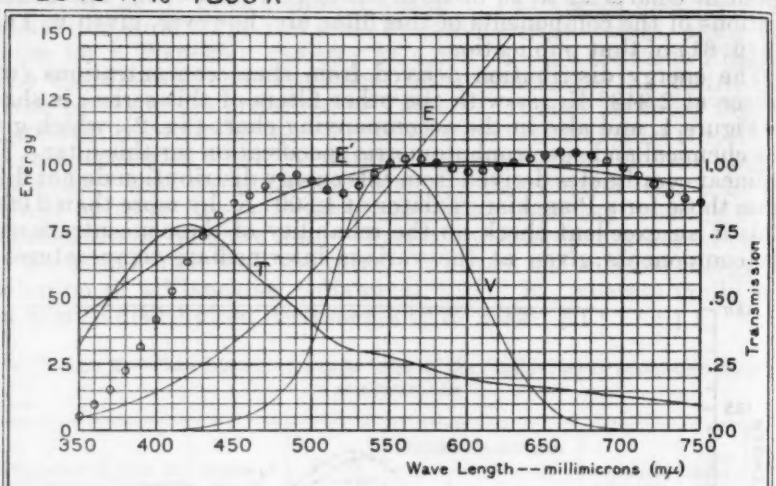


FIGURE 1.—*Relative spectral energy distribution of N. P. L. standard white compared with that for a Planckian radiator at 4,800° K. and a Davis-Gibson 2,848°-K.-to-4,800° K. source-and-filter combination.*

Table 12 referred to above. The value of the light transmission, 0.249, given on the chart, is taken from that table and not derived from independent computation.

Both of the relative spectral energy distributions produced by the respective source-filter combinations shown in Figure 1 deviate notably from that of the 4,800° K. curve. The deviations are so distributed in the case of the authors' filter, however, as to result in an accurate chromaticity match with the 4,800° K. curve according to the O. S. A. "excitation" curves. With the N. P. L. standard, on the other hand, the excess energy in the yellow-green results in failure to match the chromaticity of the Planckian radiator at any temperature, the nature and magnitude of the departure being shown in Table 2.

2848°K to 4800°K



λ (mμ)	T	E"*	E"/E'
350	0.309	5.7	.134
60	.403	9.7	.207
70	.498	15.2	.297
80	.588	22.4	.406
90	.666	31.3	.528
400	.721	41.3	.652
10	.757	52.1	.776
20	.774	63.2	.893
30	.761	73.1	.984
40	.723	80.8	1.041
450	.663	85.4	1.059
60	.601	88.3	1.059
70	.551	92.0	1.068
80	.507	95.2	1.076
90	.460	96.5	1.064
500	.404	94.2	1.017
10	.353	90.7	.962
20	.317	89.5	.934
30	.300	92.2	.949
40	.290	96.9	.986
550	.279	101.0	1.018
60	.264	102.8	1.028
70	.246	102.6	1.020
80	.227	101.0	1.000
90	.209	99.2	.980
600	.195	98.0	.968
10	.186	98.5	.974
20	.178	99.7	.987
30	.172	101.0	1.003
40	.166	102.2	1.019
650	.162	103.9	1.041
60	.157	105.0	1.058
70	.151	104.9	1.064
80	.1440	103.9	1.063
90	.1360	101.6	1.048
700	.1284	99.1	1.031
10	.1210	96.2	1.011
20	.1134	92.9	.986

Bureau of Standards. Davis-Gibson Filters

T -- Spectral Transmission of Filter at 25°C
V -- Relative Visibility Function
E -- Relative Energy of 2848°K
E' -- Relative Energy of 4800°K
E"(=T×E)* -- o o o o -- Relative Energy of 2848°K and Filter Combination

Light Transmission of Filter for 2848°K = 0.249 **

FILTER FORMULA

A

Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	2.452	grams
Mannite ($C_6H_8(OH)_6$)	2.452	grams
Pyridine (C_5H_5N)	30.0	cc
Water (distilled) to make	1000.	cc

B

Cobalt Ammonium Sulphate ($CoSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$)	21.710	grams
Copper Sulphate ($CuSO_4 \cdot 5H_2O$)	16.110	grams
Sulphuric Acid (sp. gr. 1.835)	10.0	cc
Water (distilled) to make	1000.	cc

These data are for a one centimeter layer each of solutions A and B in a double cell with three plates of borosilicate crown glass (refractive index, D line, = 1.51), each 2.5 mm thick.

* Adjusted to make sum of E" - E' from 400 to 720 mμ equal practically to zero

** Factor to be used to multiply the candle-power of the light-source to obtain the candle-power of the source-and-filter combination

FIGURE 2.—*Chart describing Davis-Gibson filter, 2,848° K. to 4,800° K.*

This filter is selected from those of Series II, B. S. Misc. Pub. No. 114. (See Table 12 of that publication.)

The superiority of the N. P. L. standard in the violet results from the higher temperature of the source used, as well as from the higher transmittancy of the filter in this region. This advantage of the higher temperature of source is, however, counteracted somewhat by the consequent shorter life of the lamp.

WASHINGTON, August 12, 1931.

ISOLATION AND DETERMINATION OF METHYLCYCLOPENTANE IN A MIDCONTINENT PETROLEUM [1] [2]

By Mildred M. Hicks-Bruun and Johannes H. Bruun [3]

ABSTRACT

This paper describes the isolation of methylcyclopentane from an Oklahoma petroleum. The petroleum was first fractionated by distillation into a series of 1° cuts. The fractions boiling between 68° and 78° C. were subjected to nitrating treatments in order to remove the benzene, which was previously found to be in these fractions as a constant boiling mixture with the hexane. The benzene-free fractions were then subjected to further distillations, after which the methylcyclopentane was isolated by a combination of equilibrium melting with distillation after admixture with methyl alcohol.

The following physical constants were determined for the isolated hydrocarbon: Normal boiling point, 71.8° C.; freezing point, −141.9° to −142.3° C.; specific gravity, 20°/4°, 0.7487; refractive index n_D^{20}, 1.4098; critical solution temperature with aniline, 34.7° C. The infra-red absorption spectrum was also determined.

The binary eutectic mixture of methylcyclopentane and *n*-hexane was found to contain 95.9 mole per cent of methylcyclopentane and to melt at −143.5° C.

The latent heat of fusion of methylcyclopentane was calculated to be 7.6 calories per gram.

From the freezing behavior the purity of the isolated sample of methylcyclopentane was found to be 98.7±0.2 mole per cent.

The largest amount of methylcyclopentane was in the fraction boiling between 71° and 72° C. This fraction consisted of about 82 weight per cent of methylcyclopentane. Based upon the crude petroleum the amount (4.5 kg) of the methylcyclopentane present was found to be about 0.2 of 1 per cent.

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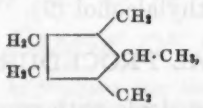
I. INTRODUCTION

Although methylcyclopentane,



is one of the lowest boiling of the so-called naphthene hydrocarbons, no one has reported its isolation from petroleum in a demonstrably

[1] This paper describes some of the results obtained in an investigation on the separation, identification, and determination of the chemical constituents of commercial petroleum fractions listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the central petroleum committee of the National Research Council.

[2] Presented before the petroleum division, American Chemical Society, Buffalo, N. Y., Sept. 1, 1931.

[3] Research associate for the American Petroleum Institute.

pure condition. One of the probable reasons for this is the fact that its boiling point (about 72° C.) is near that of *n*-hexane (69° C.), which usually predominates in this fraction. Furthermore, the methylcyclopentane molecule has a tertiary carbon atom and a consequently great reactivity toward chemical agents. Attempts to isolate this hydrocarbon from its mixture with hexane and other compounds by means of chemical reagents, such as strong sulphuric acid, chlorosulphonic acid, fuming nitric acid, and chlorine, have failed, because the methylcyclopentane would be attacked at the same rate or even more vigorously than are the other constituents.

However, the presence of methylcyclopentane in petroleum has been indicated by different investigators. By treating a Caucasian petroleum fraction (boiling point about 70° C.) with dilute nitric acid, Markownikoff (1) [4] was able to produce small quantities of a tertiary nitroproduct which he identified with the corresponding one obtained from synthetic methylcyclopentane. Mabery and Sieplein (2) chlorinated a California petroleum fraction and found a chloride which they identified as tertiary methylpentamethylenechloride. Aschan (3) oxidized a Caucasian petroleum fraction and found succinic acid as one of the products of the oxidation. From this he concluded that methylcyclopentane was present in the petroleum.

Other investigators—for instance, Young (4)—found that the fractions of a Pennsylvania petroleum distilling around the boiling point of methylcyclopentane exhibited a high specific gravity and reacted vigorously with fuming nitric acid. Chavanne (5) in his work on a Borneo petroleum found that by plotting the weights as well as specific gravities of the fractions against their boiling ranges the maxima of these curves were exhibited by the fractions distilling around the boiling point of methylcyclopentane. By plotting the critical solution temperatures of the fractions with aniline against their boiling ranges a minimum was observed at the boiling point of methylcyclopentane.

II. METHODS EMPLOYED

The isolation of methylcyclopentane from petroleum was accomplished by means of methods and apparatus which have been described in previous papers. The following of these methods were used:

(1) Fractional distillation (6).
(2) Nitration (for removal of the benzene) (7).
(3) Equilibrium melting (7, 8).
(4) Distillation with methylalcohol (9).

III. EXPERIMENTAL PROCEDURE AND RESULTS

The present investigation deals with some of the fractions which were obtained as a result of six successive distillations of 600 gallons of an Oklahoma petroleum (10).[5] The distribution of these fractions over their boiling ranges is shown by the graph in Figure 1.[6] From

[4] Figures in parentheses here and throughout the text indicate references given in the bibliography at the end of this paper.

[5] The petroleum used for this investigation was obtained from Well No. 6 of the South Ponca Field, Kay County, Okla.

[6] Acknowledgment is made to F. W. Rose, jr., for the drawing of all the figures used in this paper.

this graph it will be noted that about 6,600 g of material distilled between 70° and 73° C. The boiling point of methylcyclopentane is about 72° C.

All of the fractions were subjected to a nitrating treatment (7), in order to remove quantitatively the benzene which was present as

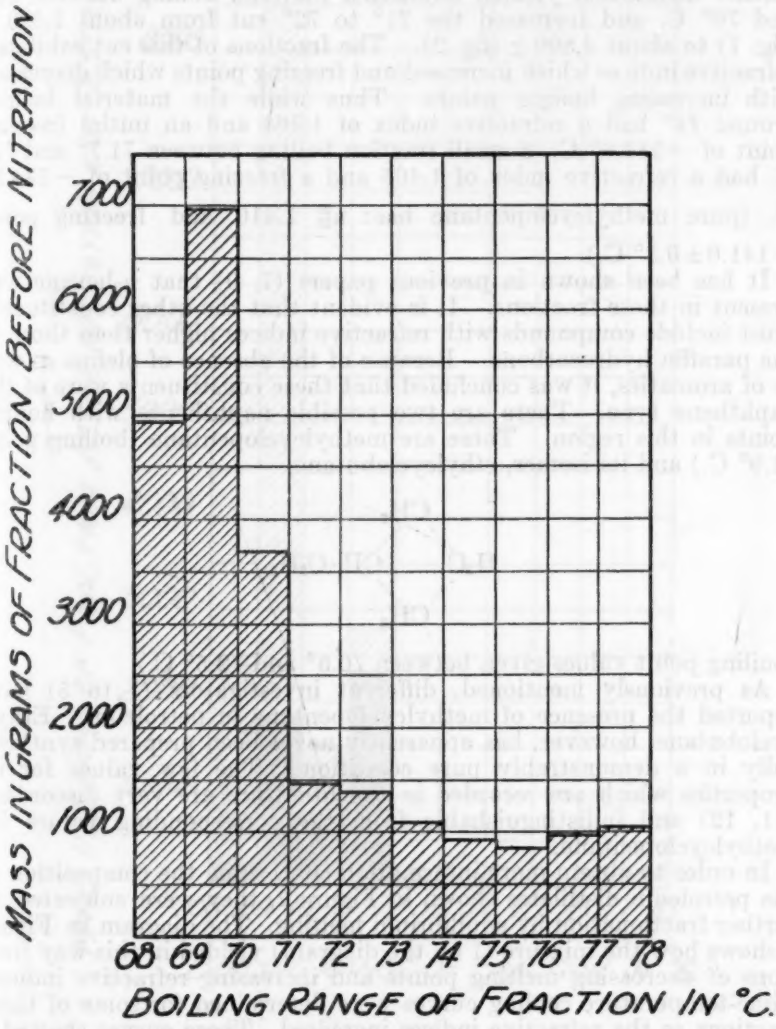


FIGURE 1.—*Distribution of the fractions over the boiling range before the removal of the benzene*

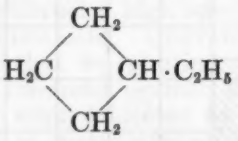
Ordinate: Mass in grams of fraction. Abscissa: Boiling range of fraction

a constant boiling mixture with the hexanes (7, 9). The benzene-free fractions were subsequently distilled four times. All of the distillations were made by S. T. Schicktanz and a staff of still operators. The boiling points of the distillates were accurately determined by means of a continuous boiling-point apparatus (7). Fractions with nearly

the same boiling points and refractive indices were mixed for further separation. After the last four distillations the fractions were redistributed, as shown by the graph in Figure 2.

By comparing Figures 1 and 2 it will be noted that the 3,700 g of material in Figure 1, with a boiling range of 70° to 71° C., by further distillation yielded additional material boiling between 69° and 70° C. and increased the 71° to 72° cut from about 1,500 g (fig. 1) to about 2,800 g (fig. 2). The fractions of this cut exhibited refractive indices which increased and freezing points which decreased with increasing boiling points. Thus while the material boiling around 71° had a refractive index of 1.394 and an initial freezing point of −111.6° C., a small fraction boiling between 71.7° and 72° C. had a refractive index of 1.405 and a freezing point of −134.3° C. (pure methylcyclopentane has: n_D^{20} 1.410 and freezing point −141.0 ± 0.3° C.).

It has been shown in previous papers (7, 9) that *n*-hexane was present in these fractions. It is evident that the other constituents must include compounds with refractive indices higher than those of the paraffin hydrocarbons. Because of the absence of olefins as well as of aromatics, it was concluded that these constituents were of the naphthene type. There are two possible naphthenes with boiling points in this region. These are methylcyclopentane (boiling point 71.9° C.) and its isomer, ethylcyclobutane,



(boiling point values given between 70.5° and 72.5° C.).

As previously mentioned, different investigators (1 to 5) have reported the presence of methylcyclopentane in petroleum. Ethylcyclobutane, however, has apparently never been prepared synthetically in a demonstrably pure condition. The few values for its properties which are recorded in the literature are very discordant (11, 12) and indistinguishable from the corresponding values for methylcyclopentane.

In order to obtain more information concerning the composition of the petroleum distillates shown in Figure 2, they were subjected to further fractionation by equilibrium melting. The diagram in Figure 3 shows how the mixture (1 on the diagram) yielded in this way fractions of decreasing melting points and increasing refractive indices. Time-temperature cooling curves were determined for some of these fractions as the refractive indices increased. These curves showed a progressive decrease in initial freezing point with increasing refractive index and the same constant eutectic break (2 in fig. 3) at −143.5° C. Fractionation by equilibrium melting was no longer effective when the refractive index of the fraction reached 1.4075. The fractions with this refractive index had narrow freezing ranges, all starting at −143.5° C., and were judged to be of eutectic composition. In order to obtain further separation, the eutectic mixture (2 in fig. 3) was subjected to distillation with the addition of methyl alcohol (9).

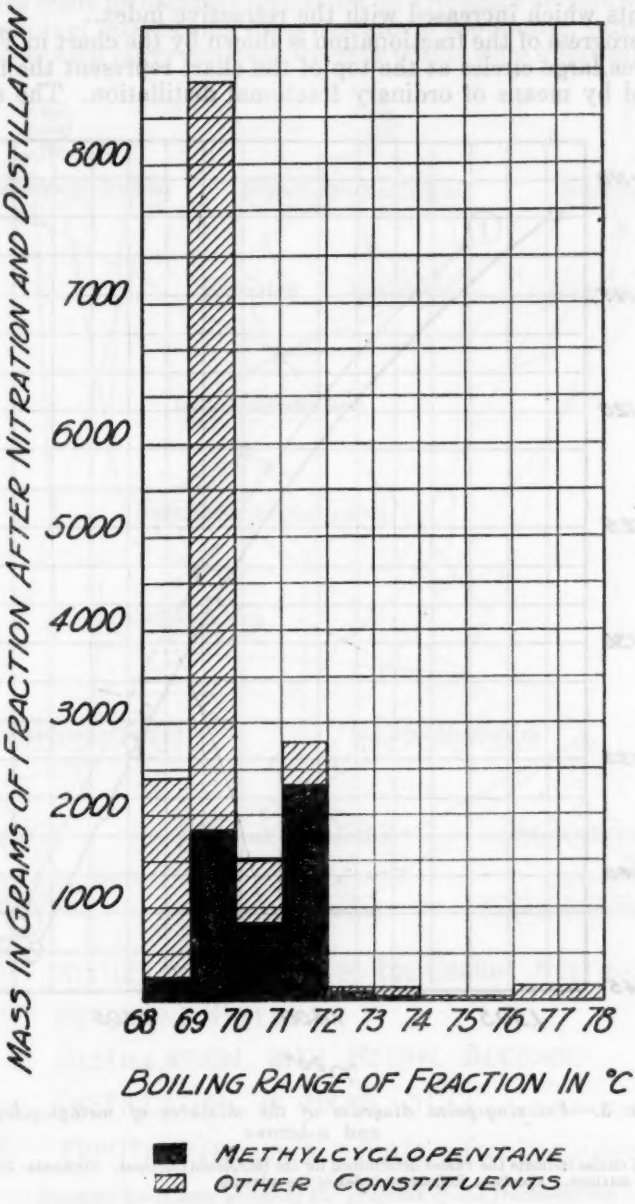


FIGURE 2.—*Distribution of the fractions over the boiling range after removal of the benzene and subsequent distillations*

The black portion of the graph indicates the amount of methylcyclopentane in the fractions. Ordinate: Mass in grams. Abscissa: Boiling range of fraction

As a result of these distillations, fractions were obtained having freezing points which increased with the refractive index.

The progress of the fractionation is shown by the chart in Figure 4. The three large circles at the top of the chart represent the fractions obtained by means of ordinary fractional distillation. The numbers

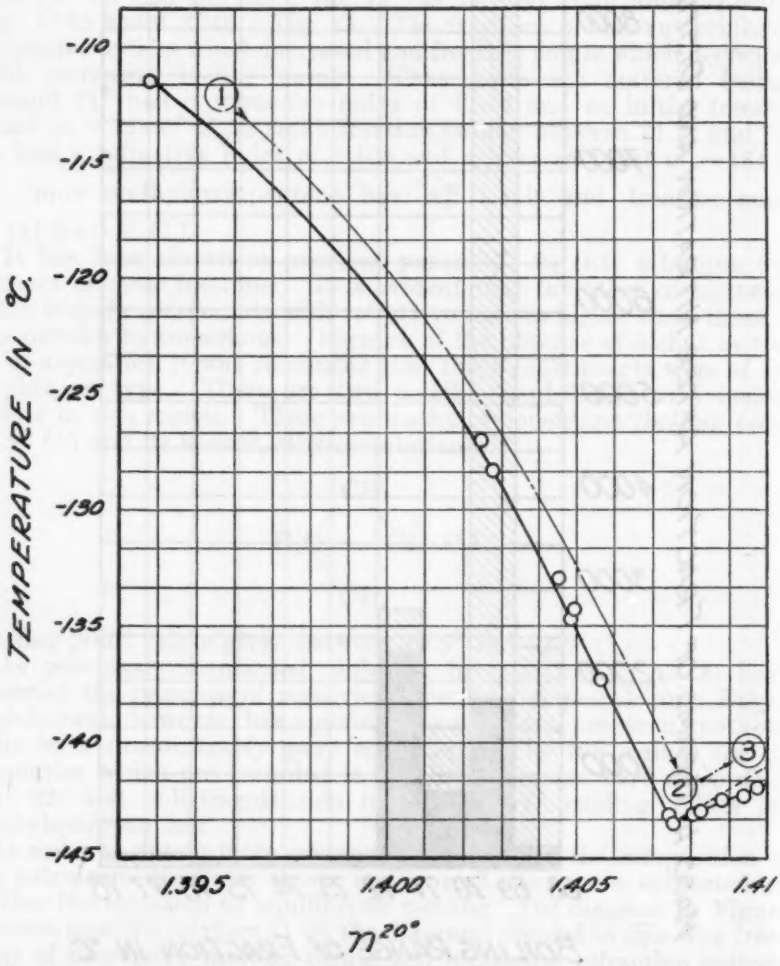


FIGURE 3.—*Freezing-point diagram of the mixtures of methylcyclopentane and n-hexane*

The small circles indicate the values determined for the petroleum fractions. Ordinate: Initial freezing point of the mixture. Abscissa: Refractive index of the mixture.

inside of the circles indicate the refractive indices of the respective fractions. The broken lines denote fractions obtained by equilibrium melting. The continuous lines show the manner in which the fractions were mixed and the dot-dash lines indicate fractionation by distillation in a 30-plate column still with the addition of methyl alcohol. The

final fractionation, indicated by crossed lines at the bottom of the chart, was made by ordinary distillation in a 60-plate column still (13).

As a result of interlocking these methods of separation, three groups of fractions with fairly constant freezing points were obtained:

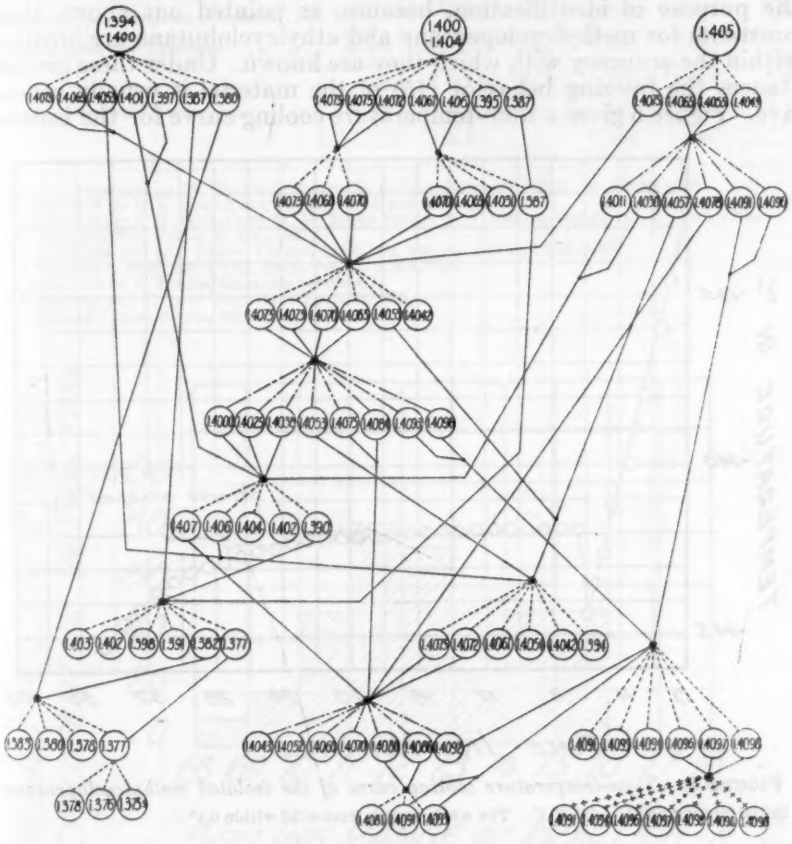


FIGURE 4.—*Chart showing the progress of the fractionation*

1. A eutectic mixture freezing at −143.5° C. This mixture consisted presumably of *n*-hexane and methylcyclopentane. (See below.)

2. A small *n*-hexane fraction with refractive index 1.3755. Further work on this fraction was dispensed with because the separation of *n*-hexane had been previously accomplished (14).

3. A fraction freezing at −141.9° C. The physical constants of this fraction were determined and were found to agree with those of pure synthetic methylcyclopentane. (See Table 1.) It should be noted, however, that the values for the refractive index, specific gravity, and boiling point are of comparatively little significance for the purpose of identification, because, as pointed out above, these constants for methylcyclopentane and ethylcyclobutane are identical within the accuracy with which they are known. Under these circumstances the freezing behavior (15) of the material is usually conclusive. Figure 5 gives a time-temperature cooling curve for the isolated

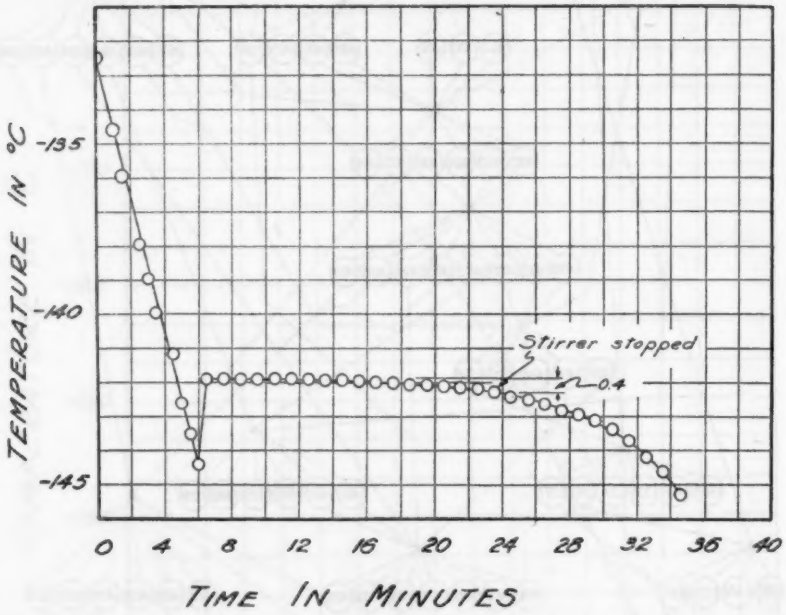


FIGURE 5.—*Time-temperature cooling curve of the isolated methylcyclopentane*
Initial freezing point: −141.9° C. The whole sample froze solid within 0.4° C.

sample. Half of it froze solid within about 0.2°. The initial freezing point −141.9° C., must therefore be lower than that of the pure hydrocarbon by about 0.4° (16). The freezing point of the latter is therefore about −141.5° C., which agrees substantially with the value −141.0° ±0.3° C. reported by Timmermans. (See Table 1.) Unfortunately, the freezing point of ethylcyclobutane is not on record, so that the above evidence for identification is not wholly conclusive. Since, however, it is extremely unlikely that both the freezing point of ethylcyclobutane and its critical temperature of solution in aniline are identical with the corresponding values for methylcyclopentane, the identification may be assumed to be substantially established.

TABLE 1.—*Physical constants of methylcyclopentane and ethylcyclobutane*

	Molecular weight	Boiling point	Freezing point	d_D^{20}	n_D^{20}	C. T. S. aniline
		°C.	°C.			°C.
Methylcyclopentane (from petroleum)	[1] 84.1 ±0.2	71.8	−141.9	[2] 0.7487	1.4098	[3] 34.7
Synthetic methylcyclopentane	84.092	[4] 72–72.2		[4] .7483	[4] 1.4088	
		[5] 72				[5] 35
		[6] 71.9	[7] −141.0 ±0.3	[6] .7482	[6] 1.4103	[6] 34.7
Synthetic ethylcyclobutane	84.092	[8] 72.2		[8] .745	[8] 1.4082	
		72.5				
		[9] 70.6		[9] .7284	[9] 1.404	

[1] Method described by M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, pp. 575–83, 1930.
[2] Determined by B. S. Section of Capacity and Density.
[3] For method see J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 612, 1931.
[4] N. Zelinsky, Ber., vol. 44, p. 2781, 1911.
[5] G. Chavanne and L. J. Simon, Compt. rend., vol. 168, pp. 1112 and 1326, 1919.
[6] G. Chavanne, Bull. Soc. Chim. Belg., vol. 31, p. 338, 1922.
[7] Determined by J. Timmermans, see reference 5.
[8] N. Zelinsky and J. Gutt, Ber., vol. 41, p. 2432, 1908.
[9] J. Kishner, Chem. Zentr., vol. 34II, p. 2132, 1913.

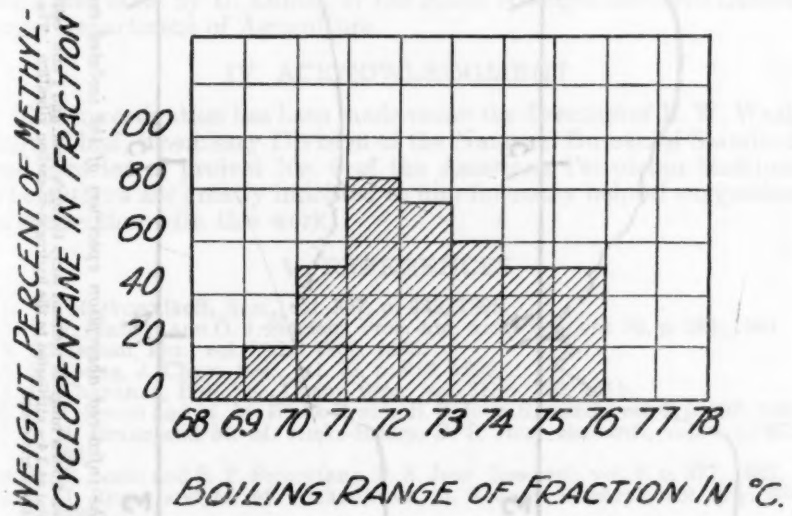


FIGURE 6.—*Amount of methylcyclopentane found in the petroleum*

Ordinate: Weight per cent of methylcyclopentane in the petroleum fraction
Abscissa: Boiling range of fraction in ° C.

On this assumption the purity of the hydrocarbon can be calculated by comparing its initial freezing point with that of pure methylcyclopentane and computing the amount of impurity required to produce the corresponding freezing-point depression. To make this calculation, the heat of fusion of methylcyclopentane is required. Since no value for this quantity is on record, an approximate and sufficiently accurate value was computed with the aid of the observed eutectic temperature of the system in the following manner (17): Since the eutectic liquid is saturated also with *n*-hexane, the melting point and latent heat of fusion of which are known, the eutectic composition was first calculated and found to be 95.9 mole per cent of methylcyclopentane. From this composition and the difference between the eutectic temperature and the freezing point of pure methylcyclopentane the value

FIGURE 7.—*The infra-red absorption spectrum of the isolated methylcyclopentane*

These curves are the energy transmission lines of emission from a tungsten filament lamp through 1 cm. and 1 mm. cells, respectively. The bands at 1.71 μ and 1.2 μ are the second and third harmonics, respectively, of the fundamental at 3.4 μ attributed to the hydrogen-to-carbon vibration. The effective slit width is about 10 A. Measured by U. Liddel, of the Fixed Nitrogen Laboratory, U. S. Department of Agriculture

7.6 calories per gram was calculated for the latent heat of fusion of methylcyclopentane. Using this value, the composition of the various methylcyclopentane fractions shown by points 2 to 3 on the diagram of Figure 3 were then calculated, as was also the composition of the best sample of methylcyclopentane isolated from the petroleum. For these calculations Timmerman's value $-141.0 \pm 0.3°$ C. was used as the freezing point of pure methylcyclopentane and the calculation gave 98.9 ± 0.2 mole per cent as the purity of the methylcyclopentane isolated from petroleum.

Figure 6 shows the weight per cent of methylcyclopentane in the petroleum fractions boiling from 68° to 78° C. From Figures 2 and 6 the amount of methylcyclopentane present in these fractions is calculated. Their distribution and mass in grams (total about 4.5 kg) are shown by the black portion of the chart in Figure 2. This is equivalent to about one-fifth of 1 per cent of the crude petroleum used and is considered to be a conservative estimate of the amount of methylcyclopentane present.

Figure 7 shows the infra-red absorption spectrum of the liquid. This work was done by U. Liddel, of the Fixed Nitrogen Research Laboratory, Department of Agriculture.

IV. ACKNOWLEDGMENT

This investigation has been made under the direction of E. W. Washburn, Chief, Chemistry Division of the National Bureau of Standards and director of project No. 6 of the American Petroleum Institute. The authors are greatly indebted to him for many helpful suggestions in connection with this work.

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6. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 607, 1931.
7. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 6, p. 872, 1931.
8. R. T. Leslie and S. T. Schicktanz, B. S. Jour. Research, vol. 6, p. 377, 1931.
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10. E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 469, Table 1, 1929.
11. N. Zelinsky and J. Gutt, Ber., vol. 41, p. 2432, 1908.
12. J. Kishner, Chem. Zentr., vol. 34II, p. 2132, 1913.
13. J. H. Bruun and S. T. Schicktanz, B. S. Jour. Research, vol. 7, pp. 851–882, 1931.
14. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 6, pp. 869–79, 1931.
15. E. W. Washburn, Ind. Eng. Chem., vol. 22, p. 985, 1930.
16. W. P. White, J. Phys. Chem., vol. 24, p. 393, 1920.
17. For the evidence justifying this procedure, see Washburn, Principles of Physical Chemistry, 2d ed., McGraw-Hill Book Co., New York, 1921, p. 206.

NOTE—While the manuscript of this paper was in the hands of the printer an account of a direct experimental determination of the latent heat of fusion of methylcyclopentane appeared by H. M. Huffman, G. S. Parks and M. Barmore, J. Am. Chem. Soc., vol. 53, p. 3882; 1931.

If this experimental value, 19.5 calories per gram, is used in place of our computed value, the purity of our methylcyclopentane is calculated to be 97.2 per cent.

WASHINGTON, July 24, 1931.

THE PHOTOGRAPHIC EMULSION; THE SILVER ION-GELATIN EQUILIBRIUM

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Electrometric determination of silver ion activity in silver nitrate-gelatin solutions showed strong selective combination of silver ion with gelatin. This decreases with increasing hydrogen ion concentration, but does not vanish on the acid side of the isoelectric point. Similar measurements in silver bromide-ammonia-gelatin solutions detected no combination of gelatin with the silver-ammonia ion. The hydrolysis of silver bromide and chloride in thoroughly washed emulsions was calculated from the electrometric data and verified by direct experiment.

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I. INTRODUCTION

The buffer action of gelatin—its capacity to combine with either acids or bases and reduce the change in hydrogen ion concentration resulting from the addition of the acid or base to the solution—is well known and important in several types of photographic phenomena. The object of this paper is to call attention to a similar capacity of gelatin for combination with silver ions, and some of its photographic consequences.

It should first be pointed out that in the combination of gelatin with acids or bases, the hydrogen or hydroxyl ions are combined in a manner which may under most conditions be considered unique. When, for example, gelatin is added to a solution of hydrochloric acid, the activity of the hydrogen ion as determined by any of the well-known methods is greatly reduced, while that of the chlorine ion is unaffected in dilute solutions. If such a mixed solution is separated by a suitable membrane from water or an electrolyte solution, the behavior of the chlorine ion may be predicted on the assumption that it is held to the gelatin only by electrostatic forces, while the gelatin-hydrogen ion complex must be treated as a single new unit. This applies whether we believe with Loeb, that gelatin acts as an amphoteric electrolyte and the complex is a new ion, differing from other ions mainly by nondiffusibility, or whether we adopt the view supported by Bancroft that the gelatin units are a separate phase, to which the

hydrogen ion is selectively adsorbed. The combination with the hydroxyl ion of bases is of the same type as with the hydrogen ion and apparently of about the same strength. On the alkaline side of the isoelectric point, the gelatin-hydroxyl ion complex will therefore hold any available cation at least electrostatically. Loeb [1] has given striking qualitative demonstrations of these phenomena. Using the photochemical reduction of silver ion by gelatin as a test for its presence, it is readily shown that this ion can be washed completely out of gelatin on the acid side of the isoelectric point, but is retained at pH greater than 4.7.

Recent investigations have disclosed numerous cases in which this simple treatment is invalidated by appreciable combination of other ions with the gelatin in such a manner as to reduce their activity. The combination with cations extended well to the acid side of the isoelectric point, and that of the anions to the alkaline side. Northrop and Kunitz [2] have furnished the most data on this subject, using concentration cells, and an ingenious method based on the measurement of membrane potential for those ions for which no electrode was available.

Most of their measurements were made at the isoelectric point, where no combination of the gelatin with any ion is to be expected on the simple theory, but they also studied the effect of varying hydrogen ion concentration. No combination of Na^+ or K^+ was detected, but a single determination with silver nitrate showed appreciable combination of the silver ion. All the bivalent cations tested (Cu^{++}, Ca^{++}, and Mg^{++}) were found to combine with the gelatin in amounts varying with their concentration and the pH, up to 9×10^{-4} gram equivalents per gram of gelatin. This maximum not only agrees with that obtained by Hitchcock [3] for hydrogen, but in mixtures of copper salts and acids the total of combined hydrogen and copper ions was approximately constant at this value. The combined copper was appreciable even at pH 2, although for the same activity it was very much less than the combined hydrogen. The maximum combination with both copper and hydrogen was reduced to 5×10^{-4} gram equivalent per gram of gelatin by deaminizing. Al^{+++} and La^{+++} reached a maximum of about 5×10^{-4} gram equivalent per gram gelatin, although the measurements were carried up to molar solutions; this, like the equivalence of hydrogen and copper, is strong evidence for true chemical combination, since the adsorption of trivalent ions would be expected to be greater than that of bivalent ions.

The measurements with copper were not carried to the alkaline side of the isoelectric point, but those with calcium covered a range of pH 2.5 to 10. Northrop and Kunitz state that "the value (of combined calcium) rises rapidly as the solution becomes less acid and remains approximately constant on the alkaline side of pH 4.7," but to the writers their data are more consistent with a continuous increase with pH.

No combination of nitrate or sulphate ion was detected, but combination with chloride ion up to 3×10^{-4} gram equivalent per gram

[1] Loeb, Proteins and the Theory of Colloid Behavior.
[2] Northrop and Kunitz, J. General Physiology, vol. 7, p. 25, 1924; vol. 9, p. 351, 1926; vol. 11, p. 481; 1928.
[3] Hitchcock, J. General Physiology, vol. 12, p. 495; 1929.

of gelatin was reported in the more concentrated solutions (0.1 *M* or more).

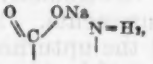
The combination of silver ion and gelatin has been investigated in other cases. Pauli and Matula,[4] using concentration cells, found depression of silver ion concentration on adding gelatin, but their gelatin was not deashed and they give no data on pH.

There have been two investigations in photographic laboratories. Rawling and Mitchell,[5] working on methods of determination of soluble bromide in emulsions, found that they extracted more than should have been present. The effect was greater in silver chloride emulsions and absent in those of silver iodide. They infer from this the existence of a silver gelatin complex in amounts varying with the silver ion concentration.

Schmidt and Pretschner,[6] after numerous analyses of photographic emulsions for nonhalide silver, have concluded that the excess silver found in thoroughly washed emulsions was formed during the washing process. They found that the excess was proportional to the solubility of the silver halide, and postulate an equilibrium between the silver halide and silver-gelatin complex depending on the relative solubilities.

One explanation for selective combination of silver ion with gelatin lies in the stability of silver ion-amino complexes. Northrop and Kunitz[7] predicted the combination of copper ion with gelatin on this basis, and apparently had the same idea in mind in their reference to the "expected" combination with silver ion. If this theory is correct, there should be no selective combination of the $Ag(NH_3)_2^+$ ion with gelatin, since the affinity of the silver for amino nitrogen is satisfied. This prediction was verified by experiment. If the analogy with the silver ammonia complex is complete, it involves combination of neutral gelatin molecules with silver ions, to form new positively charged complexes. The effect of hydrogen ion concentration would then be ascribed to a change in the free NH_2 groups with which the silver combines. Assuming the existence of peptide linkages

in the gelatin, which might be opened by alkali to form



the effect would be in the right direction.

Another alternative is the formation of a silver gelatinate entirely analogous to the sodium gelatinate of Loeb's theory, but distinguished from it by insolubility. The coagulation of proteins by silver salts is evidence for this view. Silver gelatinate would be subject to hydrolysis decreasing with increasing alkalinity. Its existence on the acid side of the isoelectric point is inconsistent with the simple theory as developed by Loeb. However, the isoelectric point represents an

[4] Pauli and Matula, Biochem. Zeit., vol. 80, p. 187; 1917.
[5] Rawling and Mitchell, Proc. 8th Int. Cong. of Phot. Abstract in Phot. Ind. vol. 29, p. 905; 1931.
[6] H. H. Schmidt, Proc. 8th Int. Cong. of Phot. Abstract in Phot. Ind. vol. 29, p. 906; 1931.
[7] See footnote 2.

equality between the two forms of ionized gelatin; it is not necessarily true that both are equal to zero. It is possible that they are in an equilibrium like the ions of water, with a rapid change in proportions at the isoelectric point like that of the ions of water at the neutral point.

II. EQUILIBRIUM IN GELATIN-SILVER NITRATE SOLUTIONS AT VARYING HYDROGEN ION CONCENTRATIONS

1. APPARATUS

The combination of silver ion and gelatin was studied by making electrometric measurements of silver ion concentration in mixed solutions of gelatin and silver nitrate. Further experiments in silver bromide-gelatin emulsions, which were tested photographically as well as chemically, will be described in a separate communication.

All determinations were made at 30.0° C., using a simple air thermostat. This was a cubical box, 2 feet on edge, lined with heat insulating board on all sides but the front. The door in the front was provided with a double glass window, coated with orange lacquer, which excluded practically all radiation of wave length less than 520 mμ. This precaution was probably unnecessary, as the cell was illuminated only by relatively dim artificial light, but for measurements of silver ion concentrations in photographic emulsions the possibility of error from photolysis was not to be disregarded. The air was circulated in the thermostat by a blower of 55 cubic feet per minute capacity. By making the bulb of the thermoregulator a grid of 10 mm tubing placed across the inlet of the blower, and using a heater of fine bare wire in the outlet tube, lag was reduced so that fluctuations as measured by a mercury thermometer were less than 0.02°; all measurements were made at 30.0° ±0.1°.

The electrical measurements were made with a Leeds and Northrup "student" potentiometer, calibrated in the resistance section of this bureau and found to be accurate to 0.1 millivolt. The galvanometer was the Leeds and Northrup type 2500e, designed for electrode work.

A 0.1 *N* calomel electrode was used for reference. This was connected to the silver electrode by a salt bridge somewhat modified from that of Clark.[8] The arrangement, which is shown in Figure 1, was designed primarily for electrometric titrations, but was found suitable for potential measurements. The calomel electrode vessel was of the Clark [9] type, but the upturned tip of the connecting tube was replaced by a short piece of heavy walled tubing, about 1.5 mm bore. This passed through a rubber stopper, along with the T tube of heavy walled 1.5 mm tubing which completed the bridge. The whole apparatus was supported so that it could be lifted and swung to one side. In making connections, the cup which fitted over the rubber stopper was nearly filled with the ammonium nitrate solution. It was then forced up until it made a tight joint with the stopper; ammonium nitrate solution was forced out through the T tube, filling it. The cell and bridge were then swung over so that the upturned tip of the bridge could be lowered into the solution under test, which was ordinarily contained in a beaker with a mechanical stirrer.

[8] W. Clark, J. Chem. Soc., p. 749; 1926.
[9] W. Mansfield Clark, The Determination of Hydrogen Ions, 2d edition, p. 194, E.

There was no indication that chloride from the calomel electrode diffused through the bridge even over a period of hours. Potentials were reproducible to less than one millivolt. They were not appreciably improved by the use of a wider (5 mm) tip on the connecting tube.

The electrodes used for the silver ion-gelatin equilibrium were 1 mm wires of pure silver, annealed and frequently cleaned with cyanide

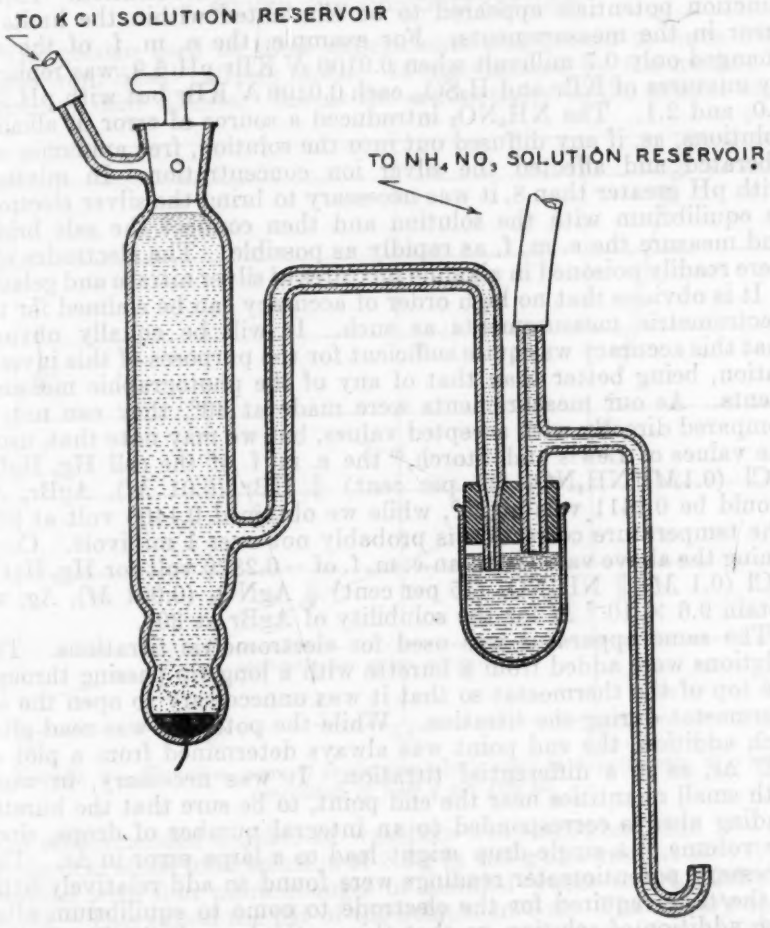


FIGURE 1.—*Calomel electrode and salt bridge for determination of silver ion concentration*

solution and hot water whenever they became appreciably sluggish. They checked within 0.5 millivolt or less. The silver wires were sealed into glass tubes with de Khotinsky cement or ceresin so that the metal was completely under the surface of the liquid. For some of the earlier work (emulsions 6–83 to 86) silver plated platinum wires were used; these were also reproducible to 0.5 millivolt, but were somewhat slower to reach equilibrium. For determinations

of bromide ion concentration in other solutions and for all measurements in emulsions, the electrodes were momentarily made anode in a dilute bromide solution and washed before use. With this treatment the electrodes reached equilibrium with the solution much more rapidly.

Fifteen per cent ammonium nitrate solution was used in the salt bridge, saturated potassium chloride being obviously out of the question for measurements of silver ion concentration. Liquid junction potentials appeared to be eliminated within the limits of error in the measurements. For example, the e. m. f. of the cell changed only 0.7 millivolt when 0.0100 *N* KBr pH 6.9, was replaced by mixtures of KBr and H_2SO_4, each 0.0100 *N* KBr but with pH 5.2, 3.0, and 2.1. The NH_4NO_3 introduced a source of error in alkaline solutions, as, if any diffused out into the solution, free ammonia was liberated and affected the silver ion concentration. In mixtures with pH greater than 8, it was necessary to bring the silver electrode to equilibrium with the solution and then connect the salt bridge and measure the e. m. f. as rapidly as possible. The electrodes also were readily poisoned in alkaline mixtures of silver nitrate and gelatin.

It is obvious that no high order of accuracy can be claimed for the electrometric measurements as such. It will be equally obvious that this accuracy was quite sufficient for the purposes of this investigation, being better than that of any of the photographic measurements. As our measurements were made at 30°, they can not be compared directly with accepted values, but we may note that, using the values of Lewis and Storch,[10] the e. m. f. of the cell Hg, HgCl, KCl (0.1*M*)‖NH_4NO_3 (15 per cent) ‖ HBr (0.01 *M*), AgBr, Ag should be 0.1411 volt at 25°, while we obtained 0.1405 volt at 30°. The temperature correction is probably not over 1 millivolt. Combining the above value with an e. m. f. of −0.2820 volt for Hg, HgCl, KCl (0.1 *M*) ‖ NH_4NO_3 (15 per cent) ‖ $AgNO_3$ (0.001 *M*), Ag, we obtain 9.6×10^{-7} *M* for the solubility of AgBr at 30°.

The same apparatus was used for electrometric titrations. The solutions were added from a burette with a long tip passing through the top of the thermostat so that it was unnecessary to open the air thermostat during the titration. While the potential was read after each addition, the end point was always determined from a plot of $\Delta E/\Delta v$, as in a differential titration. It was necessary, in work with small quantities near the end point, to be sure that the burette reading always corresponded to an integral number of drops, since the volume of a single drop might lead to a large error in Δv. The necessary potentiometer readings were found to add relatively little to the time required for the electrode to come to equilibrium after each addition of solution, so that this method was little slower than a differential titration, while it had a very real advantage in that the silver ion concentration indicated clearly the approach of the end point. This last was especially useful for titration of a solution for both bromide and chloride. The solutions were stirred continuously by a small mechanical stirrer belted to a motor outside the thermostat. The belt drive was convenient from the standpoint of space, but it was necessary to ground the stirrer carefully to avoid error from static charges.

[10] Lewis and Storch, J. Am. Chem. Soc., vol. 39, p. 2544; 1917.

Hydrogen ion concentrations were measured at 30° in the same thermostat, using a saturated calomel electrode and a bubbling hydrogen electrode. A quinhydrone electrode was also used on some of the acid mixtures. As neither can be used in the presence of silver ions, the pH of emulsions was determined colorimetrically by comparison with standard buffer solutions after the emulsions had been cleared by centrifuging.

2. SILVER ION CONCENTRATIONS

The gelatin used in these experiments was known to have been made from limed calfskin stock. It was deashed by the method of Northrop and Kunitz,[11] but as the conductivity of the gelatin after

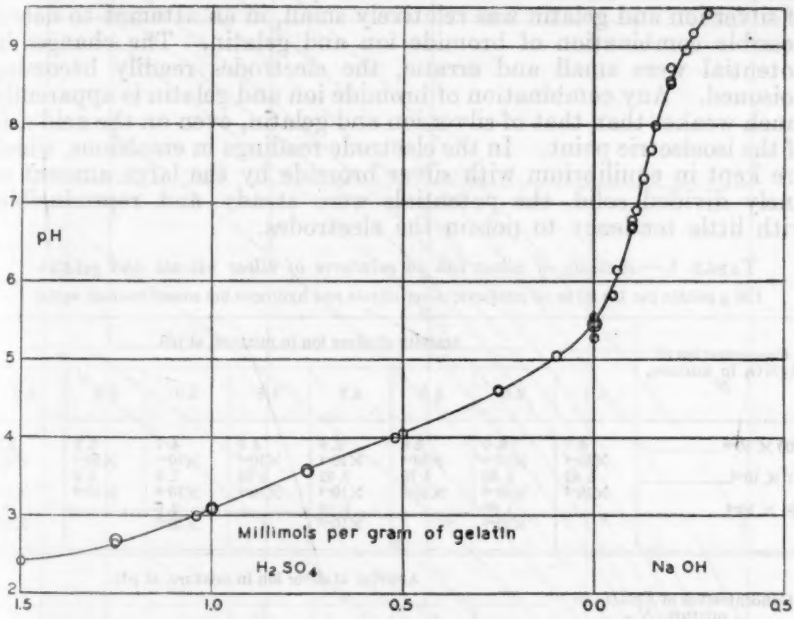


FIGURE 2.—*Titration curve of isoelectric gelatin used in experiments, at a concentration of 1.00 g per 100 ml*

the recommended number of washings was somewhat high (7×10^{-5} reciprocal ohms for a solution of 2.3 g in 100 g of water, at 30°) it was washed with four more changes of distilled water (conductivity 1×10^{-6}). This raised the pH of the gelatin to 5.4. The air-dry material was found to contain 13 per cent moisture when dried at 105° to 110°. All solutions were made up with 1.150 g of air-dry gelatin to 100 ml.

The hydrogen ion concentration was adjusted by appropriate amounts of sulphuric acid or (carbonate-free) sodium hydroxide. The titration curve is reproduced in Figure 2. Mixtures were found to be readily reproducible to less than 0.1 pH unit except on the steepest part of the curve, around pH 7, where the error may have reached 0.2.

[11] Northrop and Kunitz, J. General Physiology, vol. 11, p. 477; 1928.

The equilibrium measurements were first made on three series of mixtures, each series containing a constant amount of silver nitrate and gelatin at varying pH. Attempts to carry the measurements to higher silver concentrations (10^{-2} *N* $AgNO_3$) were unsuccessful. The electrodes were very readily poisoned, apparently by coagulated gelatin, and as the changes in concentration were smaller, the results were much less reliable. The data for silver ion activities in mixtures of 1.00 g gelatin per 100 ml over a range of pH 2.4 to 9.5 and a range of $AgNO_3$ normality 10^{-3} to 10^{-5}, are given in Table 1. Table 2 gives the data for mixtures at pH 7.0, 10^{-3} and 10^{-4} *N* $AgNO_3$ and varying gelatin concentration.

Some measurements were made on mixtures of gelatin and bromide solutions on the acid side of the isoelectric point where the combination of silver ion and gelatin was relatively small, in an attempt to detect possible combination of bromide ion and gelatin. The changes in potential were small and erratic, the electrodes readily becoming poisoned. Any combination of bromide ion and gelatin is apparently much weaker than that of silver ion and gelatin, even on the acid side of the isoelectric point. In the electrode readings in emulsions, which are kept in equilibrium with silver bromide by the large amount of finely divided solid, the potentials were steady and reproducible, with little tendency to poison the electrodes.

TABLE 1.—*Activity of silver ion in mixtures of silver nitrate and gelatin*

1.00 g gelatin per 100 ml in all mixtures; silver nitrate and hydrogen ion concentrations varied

Concentration of $AgNO_3$ in mixture, *N*	Activity of silver ion in mixture, at pH							
	2.4	3.0	3.5	4.0	4.5	5.0	5.5	6.0
1.00×10^{-3}	6.7×10^{-4}	6.0×10^{-4}	5.6×10^{-4}	5.4×10^{-4}	4.9×10^{-4}	4.1×10^{-4}	3.3×10^{-4}	3.0×10^{-4}
9.7×10^{-4}	3.42×10^{-5}	3.30×10^{-5}	2.70×10^{-5}	2.32×10^{-5}	1.53×10^{-5}	7.9×10^{-6}	3.9×10^{-6}	1.9×10^{-6}
1.04×10^{-4}	----------	1.60×10^{-6}	----------	1.14×10^{-6}	----------	2.9×10^{-7}	----------	5.1×10^{-7}

Concentration of $AgNO_3$ in mixture, *N*	Activity of silver ion in mixture, at pH						
	6.5	7.0	[7.5	8.0	[8.5]	9.0	9.5
1.00×10^{-3}	2.65×10^{-4}	2.42×10^{-4}	2.20×10^{-4}	1.55×10^{-4}	1.1×10^{-4}	4.3×10^{-5}	1.17×10^{-5}
9.7×10^{-4}	9.4×10^{-7}	6.0×10^{-7}	3.6×10^{-7}	2.4×10^{-7}	1.5×10^{-7}	8.4×10^{-8}	4×10^{-8}
1.04×10^{-4}	----------	1.45×10^{-8}	9.0×10^{-9}	5.6×10^{-9}	3.3×10^{-9}	2.1×10^{-9}	9×10^{-10}

TABLE 2.—*Silver ion activity in mixtures of silver nitrate and gelatin*

pH constant at 7.0; gelatin and silver nitrate concentrations varied

Concentration of gelatin, g per 100 ml	Silver ion activity	
	Silver nitrate 9.7×10^{-4} *N*	Silver nitrate 9.7×10^{-3} *N*
1.00	2.4×10^{-4}	6.0×10^{-7}
.50	5.1×10^{-4}	3.6×10^{-6}
.25	7.0×10^{-4}	1.65×10^{-5}
.125	7.8×10^{-4}	4.3×10^{-5}
.063	8.7×10^{-4}	6.1×10^{-5}

3. DISCUSSION

Results for both series of measurements of silver nitrate-gelatin solutions are presented in Figure 3, calculated as gram equivalents of silver combined with one gram of gelatin. In making the calculations, the silver ion concentrations have been computed from the

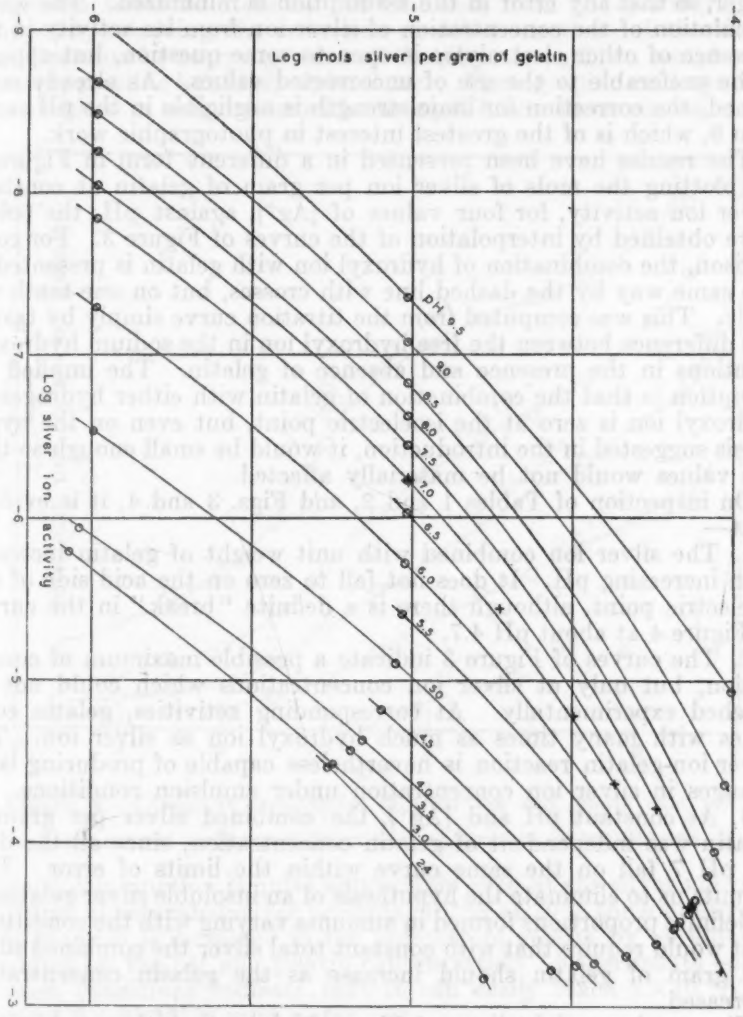


FIGURE 3.—*Combination of silver ion and gelatin at 30°. Circles represent determinations at a concentration of 1.00 g per 100 ml; crosses, determinations at other gelatin concentrations and pH 7*

activities by means of the ionic strength tables given by Lewis and Randall.[12] They were practically identical except in the more acid mixtures, which contained up to 0.015 N H_2SO_4. In making this com-

[12] Lewis and Randall, Thermodynamics, p. 382.

putation, we are using the same assumption as Northrop and Kunitz,[18] that the gelatin does not affect the ionic strength. To put it differently, the complex gelatin-hydrogen ion affects the ionic strength by the same amount as the hydrogen ion, so that it is the same in the gelatin-acid mixture as in the pure acid. In this case the contribution of the bivalent sulphate ion to the ionic strength is much the larger, so that any error in the assumption is minimized. The whole calculation of the concentration of silver ion from its activity in the presence of other electrolytes is open to some question, but appears to be preferable to the use of uncorrected values. As already mentioned, the correction for ionic strength is negligible in the pH range 5 to 9, which is of the greatest interest in photographic work.

The results have been presented in a different form in Figure 4, by plotting the mols of silver ion per gram of gelatin at constant silver ion activity, for four values of $[Ag^+]$, against pH; the points were obtained by interpolation of the curves of Figure 3. For comparison, the combination of hydroxyl ion with gelatin is presented in the same way by the dashed line with crosses, but on one-tenth the scale. This was computed from the titration curve simply by taking the difference between the free hydroxyl ion in the sodium hydroxide solutions in the presence and absence of gelatin. The implied assumption is that the combination of gelatin with either hydrogen or hydroxyl ion is zero at the isoelectric point, but even on the hypothesis suggested in the introduction, it would be small enough so that the values would not be materially affected.

On inspection of Tables 1 and 2, and Figs. 3 and 4, it is evident that—

1. The silver ion combined with unit weight of gelatin increases with increasing pH. It does not fall to zero on the acid side of the isoelectric point, although there is a definite "break" in the curves of Figure 4 at about pH 4.7.

2. The curves of Figure 3 indicate a possible maximum of combination, but only at silver ion concentrations which could not be reached experimentally. At corresponding activities, gelatin combines with many times as much hydroxyl ion as silver ion. The silver ion-gelatin reaction is nevertheless capable of producing large changes in silver ion concentration under emulsion conditions.

3. At constant pH and $[Ag^+]$, the combined silver per gram of gelatin was independent of gelatin concentration, since all the data for pH 7 fall on the same curve within the limits of error. This permits us to eliminate the hypothesis of an insoluble silver gelatinate of definite proportions formed in amounts varying with the conditions, as it would require that with constant total silver the combined silver per gram of gelatin should increase as the gelatin concentration decreased.

The nearly straight lines of Figure 3 show that the combination closely follows the adsorption isotherm. The value of 1/n is somewhat higher than usual, varying from 0.5 at pH 9 to 0.6 at pH 3. In the present state of colloid chemistry, it is hardly worth while to discuss, on the basis of the available evidence, whether this combination is to be designated as selective adsorption or as chemical combination. The silver is probably attached to the amino groups of the gelatin,

[18] Reference 2.

since the silver-ammonia ion is not adsorbed. (Sec. III of this paper.) It will be noted that the "break" in the curves of Figure 4 at the isoelectric point becomes more pronounced with increasing silver ion concentration, so that the combination more nearly approaches the prediction of the simple chemical theory.

It is probable that the decrease in silver ion activity produced by the gelatin tends to stabilize the emulsion from the photographic standpoint, retarding the reduction or other reactions of the silver ion. Reaction by rearrangement of the silver ion-gelatin complex is, of course, possible but likely to be slower. Photographic evidence will be considered in connection with the equilibrium in emulsions.

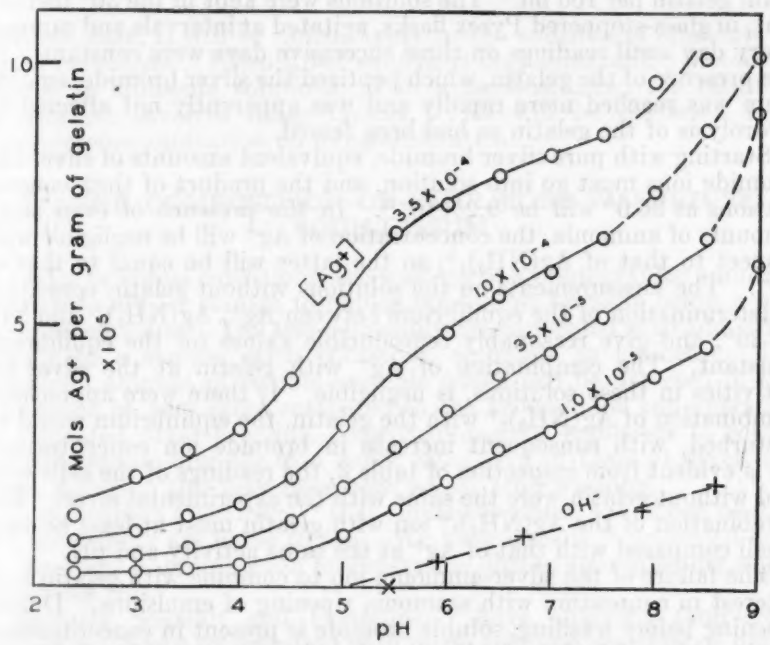


FIGURE 4.—*Change in combination of silver ion and gelatin with pH*

Crosses represent combination of hydroxyl ion and gelatin, on one-tenth the scale

As the combination is quite appreciable even at the silver ion concentration of saturated silver bromide ($10^{-6}N$ at 30°), the solubility of silver bromide is increased in the presence of gelatin by an amount depending on the pH and gelatin concentration. Experiments under emulsion conditions indicate that it can easily reach $4\times10^{-5}N$ as against $1.0\times10^{-6}N$ in pure water.

III. EQUILIBRIUM IN SILVER BROMIDE-AMMONIA-GELATIN SOLUTIONS

Since ammonia is added to many emulsions for the purpose of accelerating the ripening process, the equilibrium between the gelatin and the dissolved silver salts is of considerable interest. This was also investigated by e. m. f. measurements in the same apparatus, as

it was found reliable readings for bromide ion concentration could be obtained in the presence of ammonia provided that care was taken to keep the solution saturated with silver bromide. A small closed cell, without stirrer, was found to be satisfactory. The assumption is made that the presence of the ammonia does not change the solubility product of silver bromide, that is, that there is no change of solvent. This appears to have been justified.

The necessary data, which are given in Table 3, consisted simply of determinations of the bromide ion concentration in ammonia solutions of varying concentrations, saturated with silver bromide. The solutions were made up in pairs, with and without the addition of 1.00 gram gelatin per 100 ml. The solutions were kept in the 30° thermostat, in glass-stoppered Pyrex flasks, agitated at intervals and sampled every day until readings on three successive days were constant. In the presence of the gelatin, which peptized the silver bromide, equilibrium was reached more rapidly and was apparently not affected by hydrolysis of the gelatin as had been feared.

Starting with pure silver bromide, equivalent amounts of silver and bromide ions must go into solution, and the product of their concentrations at 30.0° will be 9.2×10^{-13}. In the presence of even small amounts of ammonia, the concentration of Ag^+ will be negligible with respect to that of $Ag(NH_3)_2^+$, so the latter will be equal to that of Br^-. The measurements on the solutions without gelatin constitute a determination of the equilibrium between Ag^+, $Ag(NH_3)_2^+$ and NH_3 at 30°, and give reasonably reproducible values for the equilibrium constant. The combination of Ag^+ with gelatin at the silver ion activities in these solutions, is negligible. If there were appreciable combination of $Ag(NH_3)_2^+$ with the gelatin, the equilibrium would be disturbed, with consequent increase in bromide ion concentration. As is evident from inspection of table 3, the readings of the cells with and without gelatin were the same with the experimental error. The combination of the $Ag(NH_3)_2^+$ ion with gelatin must at least be very small compared with that of Ag^+ at the same activity and pH.

The failure of the silver-ammonia ion to combine with gelatin is of interest in connection with ammonia ripening of emulsions. During ripening before washing, soluble bromide is present in concentrations of the order of 0.02 to 0.1*N*; the silver ion concentration is correspondingly small ($10^{-9}N$ or less, depending on temperature). Adding ammonia under these conditions, the amount of silver bromide which can go into solution is negligible with respect to the soluble bromide present; the bromide and silver ion concentrations are therefore practically unchanged. The silver ion bound to gelatin will increase because of the increased alkalinity, but must remain very small. The increased solubility of silver bromide results in increased rate of change of grain size, but the silver-ammonia ion is quite unlikely to undergo direct reaction to silver or silver sulphide. The increased rate of formation of sensitizing nuclei in the presence of ammonia is therefore to be ascribed to the increased alkalinity.

TABLE 3.—*Equilibrium at 30.0° in ammonia solutions saturated with silver bromide, with and without gelatin*

Ammonia concentration N	E. m. f. of cell (silver electrode negative)	Bromide-ion concentration	Equilibrium constant $\frac{[Ag^+]\times[NH_3]^2}{[Ag(NH_3)_2^+]}$	E. m. f. of cell with gelatin
	Volts			*Volts*
0.05	0.0366	1.75×10^{-4}	7.5×10^{-8}	0.0365
.10	.0550	3.5×10^{-4}	7.4×10^{-8}	.0539
.20	.0726	7.0×10^{-4}	7.5×10^{-8}	.0716
.40	.0909	1.41×10^{-3}	7.3×10^{-8}	.0887
.80	.1082	2.73×10^{-3}	7.9×10^{-8}	.1064

These data, it will be noted, apply to the addition of ammonia to liquid emulsions. When dried emulsions on photographic plates are bathed in ammonia solutions, as in hypersensitizing, the resulting equilibrium involves other factors. This will be discussed in a separate communication on hypersentization.

IV. THE COMPOSITION OF EMULSIONS WASHED TO EQUILIBRIUM

Under practical conditions, the washing of a photographic emulsion is carried only far enough to reduce the soluble bromide below a predetermined value. The test commonly recommended is to add silver nitrate to a sample, with potassium chromate as indicator. The minimum amount of soluble bromide which can be detected in this way must be very large compared to the bromide-ion concentration of saturated silver bromide. Most commercial emulsions as coated contain soluble bromide in a molar ratio 3–10 to 1,000 of silver bromide, although this may have been added after washing.

It is common knowledge [14] that emulsions which have been washed too thoroughly are liable to fog. We have already [15] presented data on the effect of bromide-ion concentration during after-ripening which illustrates this.

Recently Schmidt and Pretschner [16] have analyzed thoroughly washed emulsions by digestion with nitric acid and gravimetric determination of the soluble silver in the filtrate. They originally considered that this was metallic silver, formed by reduction of the silver halide during the preparation of the emulsion, but correctly decided that it could not be identified with the ripening nuclei, since there was no correlation between the amount of excess silver and the sensitivity. They have since,[17] on the basis of other evidence, realized that the silver was not present as metal but in combination with the gelatin. They found that the amount of excess silver increased with the solubility of the silver salt. Recalculating their results reported in reference 16 to gram equivalents of silver per gram of gelatin, on the assumption that their emulsions contained about 1.6 grams gelatin per gram of silver bromide, they found that the excess silver varied from zero in silver iodide emulsions to 3 to 4 $\times$ 10^{-6} in silver bromide

[14] Wall, Photographic Emulsions, p. 145. Eder-Wentzel, Die Fabrikation der photographischen Platten * * *, p. 127.
[15] Carroll and Hubbard, B. S. Jour. Research, vol. 7, p. 219; 1931.
[16] Schmidt and Pretschner, Zs. wiss. Phot., vol. 25, p. 293; 1928.
[17] Reference 6.

emulsions, and 2×10^{-5} in silver chloride emulsions. They used 700 g samples of emulsion "noodles," which had been washed 10 hours in running tap water, then 24 hours in distilled water, the washing being continued 4 to 5 hours after the washings gave no turbidity with silver nitrate. This is much more thorough than any practical emulsion washing, but as the emulsion was in "noodles" several mm. thick, it is almost certain that it did not reach complete equilibrium with the wash water.

In their most recent communication,[18] which is available only in abstract, they report that on sufficiently long washing the excess silver tended to decrease; this was not observed in any of the experiments in this laboratory. This was attributed to the difference in solubility of the silver halide grains of commercial brom-iodide emulsions, produced by differences in size and composition. The effect of size per se seems unlikely to be appreciable, but the smaller and larger grains of a brom-iodide emulsion differ widely in percentage of iodide [19] in such a way that the size effect may be enormously accentuated. However, even the smallest and most soluble grains would be removed only on very extensive washing.

If pure silver bromide dispersed in a gelatin jelly is allowed to come to equilibrium with water, the resulting bromide-ion concentration will be higher than that of saturated silver bromide, since silver ion will combine with gelatin, and the equivalent amount of bromide ion will remain in solution. The silver ion in combination with the gelatin will, therefore, be less than corresponds to the silver-ion concentration of saturated AgBr. If the wash water is repeatedly changed, removing the soluble bromide, the gelatin will ultimately come to equilibrium with the silver-ion concentration of saturated silver bromide, and further washing will remove Ag^+ and Br^- in equivalent amounts. At 30° and pH 7, for example, this corresponds to 1.2×10^{-5} g equivalents of Ag^+ per g of gelatin; the amount will vary with the temperature and pH.

Our first experiments on the effect of continued washing on the excess of silver over bromide were made to check the results of Schmidt and Pretschner, and the emulsions were extracted with 3 per cent HNO_3 according to their method. Working with the emulsion stripped from 5 by 7 inch plates, electrometric titration of the extract with 0.0010 *N* KBr was substituted for gravimetric analysis, with complete satisfaction.

It was found, in this way, that both with commercial and experimental emulsions, the excess silver became constant only after plates had been washed in running tap water for about 20 hours; washing is obviously much more rapid in the very thin coating of a plate than in emulsion noodles. The constant value obtained this way was 1.4 to 1.5×10^{-5} g equivalent Ag^+ per g gelatin, at a pH of 8 to 8.5. This amounts to 0.4 per cent of the total silver in the plate.

It was later found [20] that the excess silver could be determined by extraction with dilute acid, or by simply acidifying the stripped emulsion to pH 2 to 3, thus reducing the silver ion-gelatin combination and making a direct electrometric titration without extraction.

[18] Reference 6.
[19] Renwick and Sease, Phot. J., vol. 64, p. 360; 1924.
[20] Preliminary note in Technical News Bulletin of Bureau of Standards, September, 1930. Details will be given in a separate communication on analysis of emulsions for excess silver or bromide.

This method was used in further washing experiments which gave a satisfactory check with the equilibrium values obtained in solution.

Experimental emulsions were made up with pure silver bromide and chloride and coated in known amounts per unit area. The plates were washed for 48 hours in running tap water and for 24 hours in frequent changes of distilled water, both at 20°. The stripped emulsions were then acidified and titrated, using 0.0010 *N* KBr for the bromide emulsion and 0.010 *N* KCl for the chloride emulsion.

At 20° the silver-ion concentration of saturated silver bromide is 5.5×10^{-7} *N*; at this concentration and pH 8 gelatin is in equilibrium with 1.4×10^{-5} g equivalent Ag^+ per g (Figure 3). In the washed plates, the values found by titration were 1.79, 1.76×10^{-5}. Similarly, for saturated silver chloride at 20°, the silver-ion concentration is 1.05×10^{-5} *N*; the Ag^+ per g gelatin at pH 8 is 4.1×10^{-5} g equivalents by Figure 3 and 3.2, 3.1×10^{-5} by titration of the washed plates.

V. SUMMARY

1. The equilibrium between silver ion and gelatin has been studied by the silver electrode over a considerable range of silver and hydrogen-ion concentrations. Gelatin may cause large changes in silver-ion concentrations under conditions similar to those in photographic emulsions.

2. No combination of gelatin with the silver-ammonia ion was detected.

3. Prolonged washing of silver bromide or chloride gelatin emulsions causes appreciable hydrolysis of the silver halide, leaving the emulsion with analytically detectable excess silver in combination with the gelatin.

WASHINGTON, September 22, 1931.

A GENERAL FORMULA FOR THE COMPUTATION OF COLORIMETRIC PURITY

By Deane B. Judd

ABSTRACT

The formula for purity is called general because if the trilinear coordinates of any color referred to any given set of primary color processes and any basic stimulus be given, the colorimetric purity of this stimulus may be computed with respect to any heterogeneous stimulus as the fixed stimulus of homo-heterogeneous analysis. The derivation of the formula is given and five special cases of historical and practical interest are worked out in order to demonstrate that previous formulas for the computation of colorimetric purity and an allied ratio are special cases of this one. The connection is also given between colorimetric purity and the allied ratio variously known as saturation, saturation fraction, and Sättigung.

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I. INTRODUCTION

The definition of colorimetric purity in American literature and the methods of computing it have been fairly uniform, perhaps due to the comparative recency of its introduction in this country. Abroad, however, a number of allied concepts are variously known by this name, and this concept given, in addition, various other names. Discussion of these concepts, and indeed attempts to provide nomenclature adequate for discussion, have been handicapped by lack of more than fragmentary knowledge of the properties of the concepts, their interrelations and their dependence on choice of coordinate system. It is the purpose of the present paper to supply this lack by deriving a general formula which embraces all these allied concepts in a general system of coordinates.

II. THE PROBLEM

The tristimulus mode of specifying colors has long been recognized as the fundamental one. According to this mode a color is specified by giving the amounts of three stimuli whose mixture is requisite to produce it. The particular three stimuli in terms of which other stimuli are expressed according to the colors they evoke are called primary stimuli and the colors evoked by them are called primary colors. The choice of primary stimuli is virtually unlimited; for example, many groups of three spectrum stimuli may be chosen, or stimuli produced by means of source-and-filter combinations may be

substituted for any or all of the spectrum stimuli. The change from one set of primaries to another is merely equivalent to a change in coordinate system. The formula for colorimetric purity to be derived holds for any choice of primaries; that is, the transformation from one coordinate system to another is implied in the formula itself.

Let ρ, γ, β be the O. S. A. "excitation" curves. These functions of wave length specify the spectrum colors in terms of a certain choice of primaries according to an hypothetical observer whose characteristics are known to approximate satisfactorily those of average, normal vision.[1] The O. S. A. "excitation" curves are distinguished by their simplicity from the infinite number of other sets of curves which may represent the characteristics of the same hypothetical observer; that is, none of the ordinates of these distribution curves is less than zero, and many are zero. Any one of these infinite number of other sets of curves, say χ, ψ, ζ, may be computed from ρ, γ, β as follows:

$$\left.\begin{aligned}\chi &\equiv K_1\rho + K_2\gamma + K_3\beta\\ \psi &\equiv K_4\rho + K_5\gamma + K_6\beta\\ \zeta &\equiv K_7\rho + K_8\gamma + K_9\beta\end{aligned}\right\} \quad (1)$$

where K_1 to K_9 are arbitrary constants such that:

$$\begin{vmatrix} K_1 K_2 K_3\\ K_4 K_5 K_6\\ K_7 K_8 K_9\end{vmatrix} \neq 0 \quad (2)$$

Define:

$$\left.\begin{aligned}\bar{\chi} &\equiv \int_0^\infty \chi ET d\lambda\\ \bar{\psi} &\equiv \int_0^\infty \psi ET d\lambda\\ \bar{\zeta} &\equiv \int_0^\infty \zeta ET d\lambda\end{aligned}\right\} \quad (3)$$

where E is the spectral distribution of energy of the source used and T is the spectral transmission (or spectral reflectance in case of a reflecting surface) of the sample which the source illuminates. The product, ET, as a function of wave length is the spectral distribution of energy, therefore, of the stimulus whose colorimetric purity is to be computed [2] by recourse to the mixture data of ρ, γ, β. The numbers, $\bar{\chi}$, $\bar{\psi}$, $\bar{\zeta}$, may be used to specify the color evoked by the stimulus specified by ET because all stimuli for which $\bar{\chi}$, $\bar{\psi}$, $\bar{\zeta}$ are identical produce identical colors within the visual mechanism specified by ρ, γ, β.[3]

Define:

$$\left.\begin{aligned}X &\equiv \chi/(\chi+\psi+\zeta)\\ Y &\equiv \psi/(\chi+\psi+\zeta)\\ Z &\equiv \zeta/(\chi+\psi+\zeta)\end{aligned}\right\} \quad (4)$$

---

[1] For the sake of being specific we take the O. S. A. "excitation" curves in the form extrapolated by Priest and Gibson (J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 10, p. 230, 1925); but we might nearly as well have taken the O. S. A. "excitation" curves in their original form (J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 6, p. 548, 1922) or some other set of curves which yield a satisfactory approximation to average, normal vision.

[2] If the stimulus whose colorimetric purity is to be computed were radiant energy direct from a light source, a single symbol would naturally be used for ET. Since most stimuli whose purities are to be computed are reflected or transmitted energies, it is convenient to use the product, ET.

[3] D. B. Judd, Reduction of Data on Mixture of Color Stimuli, B. S. Jour. Research, vol. 4, pp. 515-548; 1930.

X, Y, Z are called the trilinear coordinates of the spectrum; they refer to some set of three primary processes and some basic stimulus [4] which may be inferred from the values of the constants, K_1 to K_9, of relations (1) and (2).

Define:

$$\left.\begin{aligned} x &\equiv \bar{\chi}/(\bar{\chi}+\bar{\psi}+\bar{\zeta}) \\ y &\equiv \bar{\psi}/(\bar{\chi}+\bar{\psi}+\bar{\zeta}) \\ z &\equiv \bar{\zeta}/(\bar{\chi}+\bar{\psi}+\bar{\zeta}) \end{aligned}\right\} \tag{5}$$

The numbers, x, y, z, are called the trilinear coordinates of the color evoked by the stimulus of spectral energy distribution, ET; these trilinear coordinates are referred to the same primary color processes and basic stimulus as X, Y, Z of relation (4).

When the energy of a stimulus is confined to a range of wave lengths, $\lambda-\Delta\lambda$ to $\lambda+\Delta\lambda$, so restricted that reduction of $\Delta\lambda$ makes no difference in the chromaticity of the evoked color, this stimulus is called homogeneous radiant energy of wave length, λ. Homogeneous radiant energy, E_λ, may be colorimetrically specified from relation (3) by the definite integrals:

$$\int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} \chi E_\lambda d\lambda, \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} \psi E_\lambda d\lambda, \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} \zeta E_\lambda d\lambda,$$

which for brevity are written hereafter as: $\bar{\chi}_\lambda$, $\bar{\psi}_\lambda$, $\bar{\zeta}_\lambda$. Note that these three values are proportional to: χ, ψ, ζ, for the wave length, λ.

Heterogeneous radiant energy of spectral distribution, E_w, is specified colorimetrically from relation (3) by the definite integrals:

$$\int_0^\infty \chi E_w d\lambda, \int_0^\infty \psi E_w d\lambda, \int_0^\infty \zeta E_w d\lambda,$$

which are abbreviated hereafter as: $\bar{\chi}_w$, $\bar{\psi}_w$, $\bar{\zeta}_w$. The subscript, w, is chosen because it suggests that the heterogeneous radiant energy is, as is usual, such as to evoke a "white" or "neutral" color.

The mixture of homogeneous radiant energy, E_λ, with heterogeneous radiant energy, E_w, is specified colorimetrically by the three sums of these definite integrals:

$$\bar{\chi}_\lambda+\bar{\chi}_w,\ \bar{\psi}_\lambda+\bar{\psi}_w,\ \bar{\zeta}_\lambda+\bar{\zeta}_w,$$

that is, for the mixture:

$$\left.\begin{aligned} \bar{\chi} &= \bar{\chi}_\lambda+\bar{\chi}_w \\ \bar{\psi} &= \bar{\psi}_\lambda+\bar{\psi}_w \\ \bar{\zeta} &= \bar{\zeta}_\lambda+\bar{\zeta}_w \end{aligned}\right\} \tag{6}$$

[4] The basic stimulus as defined by Priest is any stimulus whose color is represented at the center of the Maxwell triangle; that is, any stimulus whose color has the trilinear coordinates (see relation (5)), $x=y=z=\frac{1}{3}$. From relation (3) we see that the basic stimulus is any stimulus whose spectral energy distribution E_b, satisfies the condition: $\int_0^\infty \chi E_b d\lambda = \int_0^\infty \psi E_b d\lambda = \int_0^\infty \zeta E_b d\lambda$. To specify a basic stimulus is a convenient way to specify the relative scale magnitudes of χ, ψ, ζ; these magnitudes could be just as rigorously specified by giving the spectral energy distribution, E_s, for which the numbers: $\int_0^\infty \chi E_s d\lambda$, $\int_0^\infty \psi E_s d\lambda$, $\int_0^\infty \zeta E_s d\lambda$, have any given relative values.

Hence, from relation (5), the trilinear coordinates of the color evoked by this mixture are:

$$\left.\begin{aligned} x &= \frac{\bar{\chi}_h + \bar{\chi}_w}{\bar{\chi}_h + \bar{\psi}_h + \bar{\zeta}_h + \bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w} \\ y &= \frac{\bar{\psi}_h + \bar{\psi}_w}{\bar{\chi}_h + \bar{\psi}_h + \bar{\zeta}_h + \bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w} \\ z &= \frac{\bar{\zeta}_h + \bar{\zeta}_w}{\bar{\chi}_h + \bar{\psi}_h + \bar{\zeta}_h + \bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w} \end{aligned}\right\} \tag{7}$$

The trilinear coordinates, x_w, y_w, z_w, of the color evoked by the heterogeneous component of the mixture are:

$$\left.\begin{aligned} x_w &= \bar{\chi}_w/(\bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w) \\ y_w &= \bar{\psi}_w/(\bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w) \\ z_w &= \bar{\zeta}_w/(\bar{\chi}_w + \bar{\psi}_w + \bar{\zeta}_w) \end{aligned}\right\} \tag{8}$$

Define:

$$L_h \equiv \bar{\rho}_h L_r + \bar{\gamma}_h L_g + \bar{\beta}_h L_b \tag{9}$$

where L_r, L_g, L_b are any constants not all zero. $\bar{\rho}_h$, $\bar{\gamma}_h$, $\bar{\beta}_h$ represent definite integrals analogous to those represented by $\bar{\chi}_h$, $\bar{\psi}_h$, $\bar{\zeta}_h$. We use the symbol, L_h (luminosity), because when $L_r/(L_r+L_g+L_b)=0.45$, $L_g/(L_r+L_g+L_b)=0.54$, and $L_b/(L_r+L_g+L_b)=0.01$, or values not greatly differing from these, L_h varies according to wave length very closely as the luminosity of the equal-energy spectrum determined experimentally.[5] We refrain from calling L_h the luminosity because L_h deserves such a name only for the special case just mentioned. Although this special case commands the major interest because of the possibility of determining it directly by experiment[6] some attention has been given another case, $L_r=L_g=L_b$, as will appear later.

It has been shown that:[7]

$$L_h = \bar{\chi}_h L_x + \bar{\psi}_h L_y + \bar{\zeta}_h L_z \tag{9a}$$

if:

$$\left.\begin{aligned} L_x &= \frac{1}{\Delta}\left[L_r\begin{vmatrix} K_5 & K_8 \\ K_6 & K_9 \end{vmatrix} + L_g\begin{vmatrix} K_7 & K_4 \\ K_9 & K_6 \end{vmatrix} + L_b\begin{vmatrix} K_4 & K_7 \\ K_5 & K_8 \end{vmatrix}\right] \\ L_y &= \frac{1}{\Delta}\left[L_r\begin{vmatrix} K_8 & K_2 \\ K_9 & K_3 \end{vmatrix} + L_g\begin{vmatrix} K_1 & K_7 \\ K_3 & K_9 \end{vmatrix} + L_b\begin{vmatrix} K_7 & K_1 \\ K_8 & K_2 \end{vmatrix}\right] \\ L_z &= \frac{1}{\Delta}\left[L_r\begin{vmatrix} K_2 & K_5 \\ K_3 & K_6 \end{vmatrix} + L_g\begin{vmatrix} K_4 & K_1 \\ K_6 & K_3 \end{vmatrix} + L_b\begin{vmatrix} K_1 & K_4 \\ K_2 & K_5 \end{vmatrix}\right] \end{aligned}\right\} \tag{9b}$$

where $\Delta \equiv \begin{vmatrix} K_1 & K_2 & K_3 \\ K_4 & K_5 & K_6 \\ K_7 & K_8 & K_9 \end{vmatrix}$, the constants, K_1 to K_9, being those of relations (1) and (2).

[5] D. B. Judd, Chromatic Visibility Coefficients by the Method of Least Squares, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 10, pp. 635-651; 1925.
[6] See footnote 9, p. 831, and footnote 11, p. 832.
[7] See footnote 3, p. 828.

Define:

$$L_m \equiv \bar{\chi} L_x + \bar{\psi} L_y + \bar{\zeta} L_z \tag{10}$$

The subscript, m, may be read, "of the mixture," and the analogous subscript, h, of relations (9) and (9a) may be read, "of the homogeneous component."

The ratio, L_h/L_m, is of particular interest in colorimetry because in the special case[8] where it is a ratio of luminosities it may be determined experimentally[9] by the methods of heterochromatic photometry, and it has been given a special name, the colorimetric purity. We may now state the problem.

Given: (1) Values of the trilinear coordinates, x, y, z, of a color produced by the mixture of a homogeneous and a heterogeneous component, (2) the trilinear coordinates, x_w, y_w, z_w, of the color evoked by the heterogeneous component alone, (3) the trilinear coordinates, X, Y, Z, of the color evoked by the homogeneous component alone, (4) the constants, K_1 to K_9, specifying the primaries and basic stimulus of the distribution curves as related to the O. S. A. "excitation" curves, and (5) the constants, L_r, L_g, L_b; required: the ratio, L_h/L_m.

III. THE SOLUTION

The derivation of the general formula has been foreshadowed by the derivation of a special case of it.[10]
From relation (9a) and definition (10) we have:

$$\frac{L_h}{L_m} = \frac{\bar{\chi}_h L_x + \bar{\psi}_h L_y + \bar{\zeta}_h L_z}{\bar{\chi} L_x + \bar{\psi} L_y + \bar{\zeta} L_z}$$

which, in virtue of relation (6), becomes:

$$\frac{L_h}{L_m} = \frac{\bar{\chi}_h L_x + \bar{\psi}_h L_y + \bar{\zeta}_h L_z}{\bar{\chi}_h L_x + \bar{\psi}_h L_y + \bar{\zeta}_h L_z + \bar{\chi}_w L_x + \bar{\psi}_w L_y + \bar{\zeta}_w L_z}$$

After the factor, $\bar{\chi}_h + \bar{\psi}_h + \bar{\zeta}_h$, abbreviated as σ, has been divided out, this ratio becomes, from definition (4):

$$\frac{L_h}{L_m} = \frac{XL_x + YL_y + ZL_z}{XL_x + YL_y + ZL_z + \frac{\bar{\chi}_w}{\sigma} L_x + \frac{\bar{\psi}_w}{\sigma} L_y + \frac{\bar{\zeta}_w}{\sigma} L_z} \tag{11}$$

From definition (4) and relations (7) and (8) it follows at once that:

$$\left.\begin{aligned} \bar{\chi}_w/\sigma &= x_w(x-X)/(x_w-x) \\ \bar{\psi}_w/\sigma &= y_w(y-Y)/(y_w-y) \\ \bar{\zeta}_w/\sigma &= z_w(z-Z)/(z_w-z) \end{aligned}\right\} \tag{12}$$

[8] See relation (9) et. seq.
[9] I. G. Priest, Apparatus for the Determination of Color in Terms of Dominant Wave-Length, Purity, and Brightness, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 8, pp. 173–200, 1924.
[10] D. B. Judd, The Computation of Colorimetric Purity, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 13, pp. 136–138; 1926.

By substituting these three values in relation (11) a solution of the problem is obtained; but this solution may be expressed more simply by taking account of the collinearity condition: [11]

$$\frac{x-X}{x_w-x}=\frac{y-Y}{y_w-y}=\frac{z-Z}{z_w-z} \tag{13}$$

which also follows from (4), (7), and (8); it states that the points (X,Y,Z), (x,y,z), and (x_w, y_w, z_w), lie on the same straight line. In virtue of relation (13), relation (11) may be written:

$$\frac{L_h}{L_m}=\frac{XL_x+YL_y+ZL_z}{XL_x+YL_y+ZL_z+F(x_wL_x+y_wL_y+z_wL_z)} \tag{14}$$

where $F=(x-X)/(x_w-x)=(y-Y)/(y_w-y)=(z-Z)/(z_w-z)$. Relation (14) is a solution of the problem since X, Y, Z, x, y, z, x_w, y_w, z_w are known and L_x, L_y, L_z may be found from relation (9b), since the constants, K_1 to K_9, and L_r, L_g, L_b are given.

IV. FIVE SPECIAL CASES

1. For routine computation of colorimetric purity at the National Bureau of Standards it has been customary to choose constants K_1 to K_9, all zero except K_1, K_5, and K_9 (which retains all the simplicity of the O. S. A. "excitation" curves), and so to adjust K_1, K_5, and K_9 that the heterogeneous stimulus is represented at the center of the Maxwell triangle; that is, the heterogeneous stimulus is chosen as the basic stimulus.[12] Hence the constants are taken so that

$$\int_0^\infty \chi E_w d\lambda=\int_0^\infty \psi E_w d\lambda=\int_0^\infty \zeta E_w d\lambda$$

which, from this special case of relation (1), may be written

$$K_1\int_0^\infty \rho E_w d\lambda=K_5\int_0^\infty \gamma E_w d\lambda=K_9\int_0^\infty \beta E_w d\lambda$$

L_x, L_y, and L_z are chosen so that L_h of relation (9a) may be taken to represent the luminosity of the equal energy spectrum;[13] hence we may write colorimetric purity, p, instead of L_h/L_m in relation (14) which becomes; since $x_w=y_w=z_w=\frac{1}{3}$:

$$p=\frac{XL_x+YL_y+ZL_z}{XL_x+YL_y+ZL_z+F(L_x+L_y+L_z)/3}$$

Since, as is permissible (see relation (9) et seq.), it is customary to set $L_x+L_y+L_z=1$, a further simplification results:

$$p=\frac{XL_x+YL_y+ZL_z}{XL_x+YL_y+ZL_z+F/3} \tag{15}$$

[11] I. G. Priest, The Computation of Colorimetric Purity, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 9, p. 520; 1924. D. B. Judd, The Computation of Colorimetric Purity, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 13, p. 138; 1926.

[12] See footnote 4, p. 829.

[13] They may be found from relation (9b) if L_r, L_g, and L_b are appropriately chosen (see relation (9) et seq.), or they may be found de novo.

where $F/3=(x-X)/(1-3x)=(y-Y)/(1-3y)=(z-Z)/(1-3z)$. Relation (15) may be recognized as a restatement of the Judd R, Judd G, and Judd B forms of purity formula[14] with obvious changes in symbology. It is also identical with other forms of purity formula previously derived (Ives, Priest, Tuckerman). A formula developed by Froelich[15] is identical with relation (15) providing L_h of relation (9a) be taken equal to her L_λ, and providing her ratio, a, determined graphically by measuring two distances on the mixture diagram, be given its analytic equivalent, $1/(1+F)$. Two formulas developed by Guild[16] also involve ratios of lengths on the mixture diagram, the ratio in the first formula given (Guild's, p. 161) being equal to $1/(1+F)$ and that in the second formula (p. 162) being equal to $1/F$. When these substitutions are made, the first formula can readily be shown to be identical with the Ives form, which has already been proven identical with relation (15); the second formula becomes relation (15) directly.

It may be remarked that the various forms of purity formula with this convention of making the heterogeneous stimulus the basic stimulus of the system arise chiefly because (1) the coordinates of any pair of the three collinear points may be taken to form the luminosity sums, as, for example, in relation (15), which takes the coordinates of the spectrum point and the "white" point; (2) the ratio of lengths may be expressed as the ratio of the segments or as the ratio of either segment to the total, as, for example, in relation (15), which uses F, the ratio of the segments; and (3) this ratio of lengths may be evaluated from any parallel projection of the line, as, for example, in relation (15), which evaluates the ratio, F, from projections onto the axes of a mixture diagram in rectangular coordinates or onto the bisectors of the angles of the equilateral triangle, or as, for another example, in Ives's formulas, which evaluate a ratio of lengths from projections onto the sides of the equilateral triangle, or as in the formulas of Froelich and Guild, which evaluate the ratios directly from the lengths themselves. The various forms of purity formula are all useful, the particular form of purity formula to be chosen depending on the nature of the problem.

2. Another choice of primary processes which tends more toward convenience for those who think in terms of the opponent-colors theory of vision (Hering) is that which takes "neutral" as one of the three primary processes. The chromatic aspect of the response is then described solely by the other two components which have negative as well as positive values, such as a red process, whose negative is green, and a yellow process, whose negative is blue. For such a choice, if further the heterogeneous stimulus be such as to evoke the "neutral" color, and if the "neutral" color be chosen as the third primary whose distribution in the spectrum is given by ζ, the constants, K_1 to K_9, of relation (1) must satisfy the condition:

$$\int_0^\infty \chi E_w d\lambda = \int_0^\infty \psi E_w d\lambda = 0$$

[14] See footnote 10, p. 831.

[15] Clara L. Froelich, Algebraic Methods for the Calculation of Color Mixture Transformation Diagrams, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 9, p. 39; 1924.

[16] J. Guild, The Geometrical Solution of Colour Mixture Problems, Trans. Opt. Soc., vol. 26, pp. 161-162; 1924-25.

which from relation (1) is equivalent to:

$$K_1\int_0^\infty \rho E_w d\lambda + K_2\int_0^\infty \gamma E_w d\lambda + K_3\int_0^\infty \beta E_w d\lambda = 0$$

$$K_4\int_0^\infty \rho E_w d\lambda + K_5\int_0^\infty \gamma E_w d\lambda + K_6\int_0^\infty \beta E_w d\lambda = 0$$

From relation (8) and the definitions of $\overline{\chi_w}$, $\overline{\psi_w}$, $\overline{\zeta_w}$, it follows that $x_w = y_w = 0$ and $z_w = 1$. Relation (14) becomes:

$$\frac{L_h}{L_m} = \frac{XL_x + YL_y + ZL_z}{XL_x + YL_y + ZL_z + FL_z} \tag{16}$$

where

$$F = (x - X)/(-x) = (y - Y)/(-y) = (z - Z)/(1 - z)$$

A further simplification is possible if K_7, K_8, and K_9 be chosen equal, respectively, to L_r, L_g, and L_b. From relation (9b) it follows that $L_x = L_y = 0$. And if still further we arbitrarily set $L_z = 1$, as is permissible, we may write:

$$L_h/L_m = Z/(Z + F)$$

If, further, L_r, L_g, and L_b, be chosen so that the ratio may be considered a luminosity ratio as in case (1), this relation may be written as a very simple formula for colorimetric purity:

$$p = (1 - 1/z)/(1 - 1/Z) \tag{17}$$

Since Schrödinger's "vierfarbentheorie" curves [17] satisfy all the conditions under which relation (17) was derived, this relation may be taken for colorimetric purity if the trilinear coordinates X, Y, Z and x, y, z are computed from those curves. The simplicity of the formula raises the question whether Schrödinger's choice of primary color processes, which were chosen because of their interest for psychophysiological speculation, might not be a favorable choice purely for the purpose of simplifying the computation of colorimetric purity. This question is discussed presently.

3. Some attention has been given to the ratio, L_h/L_m, in the special case for which $L_x = L_y = L_z$,[18] perhaps chiefly because of the relative ease with which it may be computed. Since, from relation (4), $X + Y + Z = 1$, relation (14) for this special case may be written:

$$L_h/L_m = 1/(1 + F)$$

or

$$L_h/L_m = (x_w - x)/(x_w - X) = (y_w - y)/(y_w - Y) = (z_w - z)/(z_w - Z) \tag{18}$$

Inspection of relation (18) shows that L_h/L_m for this case is the distance on the mixture diagram from the point (x, y, z) to the "white" point (x_w, y_w, z_w), divided by the distance from the "spectrum" point (X, Y, Z) to the "white" point; hence the ratio may in this case be determined quite easily from the mixture diagram directly.

[17] E. Schrödinger, Über das Verhältnis der Vierfarbenzur Dreifarbentheorie, Sitz. Akad. Wiss., Wien, IIa, vol. 134, p. 479; 1925.

[18] W. Dziobek and M. Pirani, Normung von Signalgläsern, Proc. International Congress on Illumination, Saranac Inn, pp. 818-833; 1928. I. Runge, Die Einheitsmengen im Maxwell-Helmholtzschen Farbdreieck und die Bestimmung der Farbsättigung, Zs. f. Instrumentenk., vol. 49, pp. 600-603; 1929. S. Rösch, Darstellung der Farbenlehre für die Zwecke des Mineralogen, Fortschritte d. Mineralogie, Kristallographie u. Petrographie, vol. 30, pp. 135-136; 1929.

It should be noted, however, that L_h/L_m in this case is not necessarily the colorimetric purity because L_x, L_y, and L_z have not been especially chosen to make L_h of relation (9a) proportional to the luminosity of the equal-energy spectrum. It should also be noted that this special case loses the characteristic which is the probable cause of its existence if a different choice of primaries or basic stimulus be made; that is, with certain trivial exceptions, the coefficients, L_x, L_y, L_z, in another system of coordinates would no longer be equal; hence this special case of the ratio L_h/L_m would be just as hard to compute as colorimetric purity or any other special case of relation (14).[19] The condition for the exceptions may be seen by inspection of relation (9b).

4. In order to facilitate the computation of colorimetric purity, Runge[20] has suggested another choice of constants, K_1 to K_9. For this choice the simple formula (18) just derived results in the special case of L_h/L_m which has been defined as the colorimetric purity. It is interesting to see how the choice of constants, K_1 to K_9, suggested by Runge insures that relation (18) results in colorimetric purity.

Take L_r, L_g, L_b such that L_h of relation (9) gives the distribution of luminosity in the equal-energy spectrum. This choice permits us to substitute p for L_h/L_m. Then the constants, K_1 to K_9, are chosen, all zero except K_1, K_5, K_9, which are taken as L_r, L_g, L_b, respectively. From relation (9b) it will be discovered that, for this choice, $L_x = L_y = L_z = 1$; hence it follows that relation (18) in this special case gives colorimetric purity.

According to this plan, however, the basic stimulus of the $\rho\gamma\beta$ system is taken as the heterogeneous stimulus in the $\chi\psi\zeta$ system, necessitating that:

$$\int_0^\infty \rho E_w d\lambda = \int_0^\infty \gamma E_w d\lambda = \int_0^\infty \beta E_w d\lambda$$

which, from relation (1), is equivalent to:

$$(1/L_r)\int_0^\infty \chi E_w d\lambda = (1/L_g)\int_0^\infty \psi E_w d\lambda = (1/L_b)\int_0^\infty \zeta E_w d\lambda$$

whence, from relation (8), it is evident that:

$$x_w = L_r/(L_r + L_g + L_b)$$
$$y_w = L_g/(L_r + L_g + L_b)$$
$$z_w = L_b/(L_r + L_g + L_b)$$

Since L_b in this case is about one-fiftieth of either L_r or L_g, it is evident that the "white" point (x_w, y_w, z_w) falls relatively near one side of the Maxwell triangle.[21] This consequence of Runge's choice of coordinate system is emphasized by setting, as is usual, $L_r + L_g + L_b = 1$, which permits relation (18) for this special case to be written:

$$p = (L_r - x)/(L_r - X) = (L_g - y)/(L_g - Y) = (L_b - z)/(L_b - Z) \qquad (19)$$

[19] Another way of making the same statement is that if L_x, L_y, and L_z in another system be made equal in general, the number defined by such a choice will not be identical with L_h/L_m in this special case.
[20] See footnote 18, p. 834.
[21] See Runge's fig. 2 (footnote 18, p. 834).

5. Another coordinate system has since been proposed by Judd [22] to facilitate the computation of colorimetric purity. This system avoids the close approach of the spectrum locus to the "white" point.

Take $K_2=K_3=K_7=K_8=0$, $K_4=L_r$, $K_5=L_g$, and $K_6=L_b$, where L_r, L_g, L_b, as before, are chosen so that L_h of relation (9) gives the distribution of luminosity in the equal-energy spectrum. As in case (2), it is discovered from relation (9b) that two of the three numbers, L_x, L_y, L_z, are zero; that is, in this case, $L_x=L_z=0$, $L_y=1$.

K_1, K_9 and $L_r+L_g+L_b$ are chosen so as to make E_w the basic stimulus, which, from relation (1), requires that:

$$K_1\int_0^\infty \rho E_w d\lambda = K_9\int_0^\infty \beta E_w d\lambda = L_r\int_0^\infty \rho E_w d\lambda + L_g\int_0^\infty \gamma E_w d\lambda + L_b\int_0^\infty \beta E_w d\lambda$$

Since, by this choice, $x_w=y_w=z_w=1/3$, relation (14) may be written for $y\neq 1/3$:

$$p=(3-1/y)/(3-1/Y) \tag{20}$$

An equally simple form may be written for $y=1/3$.[22]

Relation (17) is just as simple for routine computation as relation (20) provided the trilinear coordinates (x, y, z) of the mixture are at hand. The distribution curves leading up to relation (17), however, are less simple for routine computation of the coordinates, x, y, z, than those leading up to relation (20) because they embody more ordinates different from zero and because they embody negative as well as positive ordinates; hence relation (20), considering the entire computation of colorimetric purity from spectral distribution of energy, is more advantageous than relation (17).

Relation (20) is not quite so convenient for routine computation as relation (19), since it involves the finding of two reciprocals in addition to the two subtractions and one division indicated in relation (19). However, the ease with which X, Y, Z may be found from x, y, z within the coordinate system of relation (20) is generally considerably greater than for the coordinate system of relation (19) because the coordinate system of relation (20) avoids the close approach to the spectrum locus of the "white" point (x_w, y_w, z_w).[23]

If any coordinate system is to be chosen for the specific purpose of facilitating the computation of colorimetric purity, it would seem that the adoption of that leading to relation (20) would be the most advantageous in routine computation.

V. PURITY AND SATURATION

Discussion of the terms "purity" and "saturation" is facilitated by the introduction of a ratio, L_a/L_m, which is in all respects save one the same as L_h/L_m. Since this ratio is of considerably less importance than L_h/L_m, there is little interest in showing how it may be computed from one set of primaries after having been defined in terms of another, as was done with L_h/L_m. It suffices to write a relation analogous to relation (14) which will serve to define L_a/L_m,

[22] See footnote 3, p. 828.
[23] Compare Runge's fig. 2 (see footnote 18, p. 834) with Judd's fig. 5 (see footnote 3, p. 828).

where the subscript, a, is to be read "absolute" (or "basic," according to Priest) and to be understood to refer to a color represented on the edge of the Maxwell triangle:

$$\frac{L_a}{L_m} \equiv \frac{X_aL_x+Y_aL_y+Z_aL_z}{X_aL_x+Y_aL_y+Z_aL_z+F_a(x_wL_x+y_wL_y+z_wL_z)} \tag{21}$$

where $F_a \equiv (x-X_a)/(x_w-x)$ or $(y-Y_a)/(y_w-y)$ or $(z-Z_a)/(z_w-z)$. Relation (21) differs from relation (14) only by the substitution of X_a, Y_a, Z_a, respectively, for X, Y, Z. Since L_h/L_m expresses by its approach to unity the degree of approach of the color (x, y, z) to the color (X, Y, Z), the ratio, L_a/L_m, similarly gives the degree of approach of the color (x, y, z) to the color (X_a, Y_a, Z_a). The color (X, Y, Z), used as a reference in the one case, may be evoked by some portion of the spectrum; in the second case the color (X_a, Y_a, Z_a), used as a reference, is represented on an edge of the Maxwell triangle; we know, therefore, that one of X_a, Y_a, Z_a is zero.

We have seen that two special cases of the ratio, L_h/L_m, are of interest, the one in which $L_x=L_y=L_z$ and the one in which L_x, L_y, L_z are chosen, so that L_h of relation (9a) may be taken as the luminosity of the equal-energy spectrum. These two special cases also command all the attention given to the ratio L_a/L_m.

The first case yields a formula analogous to relation (18), which becomes for $x_w=y_w=z_w=1/3$:

$$L_a/L_m=(1-3x)/(1-3X_a)=(1-3y)/(1-3Y_a)=(1-3z)/(1-3Z_a)$$

which may be written:

$$L_a/L_m=1-3c \tag{22}$$

where c is x or y or z, according as X_a or Y_a or Z_a is zero. This ratio was defined by Exner [24] as "Sättigung," for the coordinate system based on the Grund-Empfindungs-Curven of König and Dieterici.[25] Exner's definition has been followed by a number of European workers. It has been recently restated as a "not wholly unnatural measure of saturation" by Schrödinger.[26]

The second case (for $x_w=y_w=z_w=1/3$) has been given by Martin[27] as one of three variables for specifying color stimuli; the ratio, L_a/L_m, is defined by a numerical example referring to Abney's "sensation" curves and is called the "saturation fraction." This second case was also mentioned later by Priest [28] incidental to the derivation of a formula for colorimetric purity; he named the ratio, L_a/L_m, for this case the "absolute purity." Still later this ratio was defined by Haschek,[29] who called it "Sättigung."

Probably two reasons may account for choosing as a reference the edges of the Maxwell triangle as in the ratio, L_a/L_m. The first is merely that the resulting formula is simpler because one of X_a, Y_a, Z_a is always zero; this is a logical extension of the motive which prob-

[24] F. Exner, Sitz. Akad. Wiss., Wien, I, vol. 119, p. 233; 1910.
[25] A. König and C. Dieterici, Die Grundempfindungen in normalen und anomalen Farbensystemen und ihre Intensitätsvertheilung im Spectrum, Zs. f. Psych. u. Physiol. d. Sinnesorgane, 4, pp. 241-347; 1893; or see A. König, Ges. Abh., Leipzig, Barth, pp. 214-321; 1903.
[26] E. Schrödinger, Müller-Pouillets Lehrbuch d. Physik, 2d ed., vol. 2, pp. 482-484; 1926.
[27] L. C. Martin, Colour and Methods of Colour Reproduction, London, Blackie, p. 133; 1923.
[28] I. G. Priest, The Computation of Colorimetric Purity, J. Opt. Soc. Am. and Rev. Sci. Inst. vol. 9, p. 509; 1924.
[29] E. Haschek, Quantitative Beziehungen in der Farbenlehre, Sitz. Akad. Wiss., Wien, IIa, vol. 136, pp. 461-468; 1927.

ably led up to relation (18) and applies with particular force to the first case which results in the simple relation (22). The second reason is the suspicion, or the delusion, or, perhaps, the hope that the edges of the Maxwell triangle of the particular coordinate system chosen possess a fundamental theoretical significance by virtue of which they deserve the dignity of being chosen as reference lines. If the primary color processes of the coordinate system were known to be processes functionally distinct somewhere within the visual mechanism, then it could be argued that every color process represented by a point outside the Maxwell triangle would be nonexistent, or imaginary. The edges of the triangle would then represent the colors which differ from an achromatic color of the same brilliance by the maximum amount possible, and hence they would form a rather natural reference locus. However, the argument by which the König Grund-Empfindungs-Curven are taken to give the distributions of the true primary processes is by no means complete. The primaries chosen by König satisfy two criteria: (1) They are a particular "red," "green," and "blue" whose hues are close to three of the four psychologically unitary hues, that is, the hues are nearly Urrot, Urgrün, and Urblau; and (2) the distribution curves for these three primary processes may be used not only to describe the mixture relations of normal vision when used all three together, but also, by disregarding the one or the other of the "red" and "green" curves, the two most common types of partial color-blindness may be described.

Now it is not necessary to assume that one distribution curve must be disregarded to account for partial color-blindness; this is merely the simplest assumption.[30] Furthermore, the König Grund-Empfindungs-Curven are not the only set of curves which satisfy the two conditions given; they are merely the simplest set which satisfy them; that is, the Maxwell triangle which they yield approaches as closely as possible to the spectrum locus as is consistent with the criteria just mentioned. Other sets of distribution curves satisfying the two conditions satisfied in the simplest possible way by the König curves would yield Maxwell triangles whose sides departed to a greater or less extent from the spectrum locus. Now if it should be desired to choose the particular triangle of these possible triangles whose sides represent the colors of the maximum saturation possible, it would be found that so far little evidence has been recorded to guide the choice. It is rather certain, however, that any triangle which touches the spectrum locus is not the right choice, because it is an accepted fact that the colors of the spectrum viewed by a chromatically rested eye are not as saturated as the colors of the spectrum viewed by an eye adapted to the complementary color. But in all the triangles used by those proposing the ratio, L_a/L_m, as of fundamental importance, the spectrum locus does touch at least one side of the triangle. Hence our knowledge of the true physiological primaries, though much too incomplete to determine them, is sufficient to make certain that the coordinate systems thus far used for the ratio, L_a/L_m, fail to give that ratio a single vestige of theoretical importance.

It may be concluded, then, that the interest attached to the ratio, L_a/L_m, like that attached to the ratio, L_h/L_m, is a purely practical

[30] For the general form of dichromasy, see H. v. Helmholtz, Physiol. Optik, 2d ed., Leipsig, Voss. pp. 458–462; 1896.

one; either ratio for any choice of L_x, L_y, L_z will serve as one of three variables by which color stimuli may be classified according to the colors they evoke in the visual mechanism defined by ρ, γ, β. The special case of L_h/L_m when L_x, L_y, L_z are so chosen that it is a ratio of luminosities is, of course, of considerably greater interest than any other special case of either L_h/L_m or L_a/L_m, because this ratio alone can be evaluated by direct measurement.[31] To this special case, therefore, it has seemed expedient to give the name "colorimetric purity," p; and since this ratio serves all the purposes served by any other special case of either L_h/L_m or L_a/L_m, there would seem to be little justification for paying any further attention to them. When the computation of colorimetric purity was not well understood it was natural that allied entities whose derivation seemed simpler should spring up. It should be evident, however, that methods of computation of colorimetric purity are now available which compare so favorably in simplicity with any of those for any of the allied entities that the argument of mere ease of computation is no longer applicable.

It has become customary in some quarters, however, (Runge, Rösch) [32] to speak of purity and saturation (Reinheit and Sättigung) interchangeably and to remark that purity (or saturation) has been computed in four different ways. If we adopt the view that at least these four special cases deserve attention, it would seem conducive to clarity in discussion to adopt separate names for them. Terms proposed by Priest [33] for these four special cases, together with an indication of their derivation, appear in Table 1. It will be noted that, according to this terminology, the most important of the concepts, colorimetric purity, would be renamed "spectral brightness purity." In spite of the fact that previous writers have frequently applied the name "saturation" ("Sättigung") to one or another of these concepts, the suggested terminology does not include that term. This conforms to the recommendations of the O. S. A. committee on colorimetry,[34] which reserve the term "saturation" to apply to the response to a color stimulus rather than to the stimulus itself. The concepts thus far dealt with may be taken as stimulus terms, because they merely serve to group together stimuli which evoke identical colors regardless of the chromatic condition of the visual mechanism.

If, however, we could compute from the trilinear coordinates of a color a number, s, satisfying the following conditions:

(a) $s = 0$ for an achromatic color,

(b) $s_1 = s_2$ for two colors appearing to be equally saturated,

then it would seem reasonable to name this number the "saturation," in which case there would be at hand a quantitative means of evaluating the concept "saturation" which is now only qualitatively defined. Now both the ratios, L_a/L_m and L_h/L_m, satisfy condition (a), providing the heterogeneous stimulus whose color is represented at the point (x_w, y_w, z_w) be so chosen as to evoke an achromatic color; but neither L_a/L_m nor L_h/L_m has been shown to satisfy condition (b). In fact, the failure of one special case of one of these

[31] See footnote 9, p. 831.
[32] See footnote 18, p. 834.
[33] Letter to Dr. M. Pirani, Aug. 21, 1929.
[34] L. T. Troland, Report of Committee on Colorimetry for 1920-21, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 6, pp. 531-538; 1922.

ratios, L_a/L_m, for $L_x=L_y=L_z$ (Exner's "Sättigung," or basic excitation purity referred to the König fundamentals as primaries) to satisfy condition (b) has been proven experimentally by Seitz.[35] Other special cases which have been proposed do not differ from this case in such a way as to repair this deficiency; and, indeed, we may conclude from Seitz's work that no special case of either ratio satisfies condition (b) at all satisfactorily; so neither of these ratios deserve the name "saturation."

A number which may prove to satisfy fairly closely both conditions (a) and (b) is $\int_o^p (dE/dp)dp$, where p is the colorimetric purity [36] of the stimulus and dE/dp is the reciprocal of the least difference in purity perceptible as a function of purity when the change in purity is made at constant brightness along some specified path on the color triangle.[37] $\int_o^p (dE/dp)dp$ may be described as the number of least perceptible differences between a color whose stimulus is of purity, p, and the color of the same brilliance whose stimulus is of purity, $p=0$. Since the saturation of a color depends nearly if not quite as much on the momentary condition of the visual mechanism as upon the stimulus itself, it is evident that we may expect the number, $\int_o^p (dE/dp)dp$, to satisfy conditions (a) and (b) only when the visual mechanism is in such a state that the stimulus for which $p=0$ evokes an achromatic color. Since the saturation of the color evoked by a stimulus is dependent on the brightness as well as the purity of the stimulus, it is further evident that we may hope for $\int_o^p (dE/dp)dp$ to satisfy condition (b) only for the brightness to which dE/dp applies. Whether with these restrictions this number really may be made to satisfy conditions (a) and (b) and deserves the name "saturation" is a matter which is plainly of considerable complexity; it has not yet been decided. An extensive quantity of experimental data has yet to be amassed before this definition of "saturation" may be more than tentatively accepted.

Before this definition, if acceptable, can be of convenient application, a way must be found of computing dE/dp from the trilinear coordinates of the color whose stimulus has a purity, p; but at least a start has already been made in this direction. Schrödinger [38] has derived an expression for dE/dp from theoretical ground; but this expression apparently has not yet been checked against experimental results. Judd [39] has discovered empirically an expression which agrees fairly well with such experimental results as are available, but the agreement is not sufficiently striking to lead to the belief that the expression is of more than temporary theoretical interest.

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[35] W. Seitz, Über die Definition der Sättigung einer Farbe nach Helmholtz und Exner und über das Ostwaldsche Farbensystem, Zs. f. Sinnesphysiol., II, vol. 54, pp. 146–158; 1922; or see Phys. Zs., vol. 23, pp. 297–301; 1922.

[36] We define this number in terms of p, but the definition could be equally well given by substituting for p any special case of either L_a/L_m or L_b/L_m.

[37] For instance, at constant dominant wave length as adopted in defining this number by Jones and Lowry (L. A. Jones and E. M. Lowry, Retinal Sensibility to Saturation Differences, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 13, pp. 25-34; 1926), who identified it with "saturation," or at constant hue, or along such a path that this number is a minimum, as adopted by Schrödinger in defining "Sättigung" (E. Schrödinger, Müller-Pouillets Lehrb. d. Physik, 2d ed., vol. 2, pp. 555-558; 1926). Schrödinger makes the not implausible assumption that this path coincides exactly with the path of constant hue. In general, there is quite a definite difference between the path of constant dominant wave length and the path of constant hue, but we need not here choose between them for the purpose of this definition, because there is no experimental evidence that the number defined on the one basis would differ at all importantly from that defined on the other.

[38] E. Schrödinger, Grundlinien einer Theorie der Farbenmetrik im Tagessehen, Ann. d. Physik (4), vol. 63, pp. 483–520; 1920; see also footnote 37, p. 840.

[39] D. B. Judd, Purity and Saturation, A Saturation Scale for Yellow, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 14, p. 470; 1927; Saturation of Colors Determined from the Visual Response Functions, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 16, p. 115; 1928.

It is evident, therefore, that our knowledge of vision still falls considerably short of a general quantitative evaluation of the response entity, saturation.

TABLE 1.—*Terminology suggested by Priest*

QUANTITY TO BE NAMED			
L_a/L_m for $L_x=L_y=L_z$	L_λ/L_m for $L_x=L_y=L_z$	L_a/L_m for $\bar{x}_\lambda L_x+\bar{y}_\lambda L_y+\bar{z}_\lambda L_z$ equal to the luminosity of the equal-energy spectrum	L_λ/L_m for $\bar{x}_\lambda L_x+\bar{y}_\lambda L_y+\bar{z}_\lambda L_z$ equal to the luminosity of the equal-energy spectrum
DESCRIPTION		DESCRIPTION	
Hueful fraction of excitation relative to the sides of the triangle.	Hueful fraction of excitation relative to the spectrum.	Hueful fraction of brightness relative to the sides of the triangle.	Hueful fraction of brightness relative to the spectrum.
SUGGESTED TERM		SUGGESTED TERM	
Basic excitation purity.	Spectral excitation purity.	Basic brightness purity.	Spectral brightness purity.

WASHINGTON, D. C., May, 1931.

VARIATION OF PHOTOGRAPHIC SENSITIVITY WITH DIFFERENT LIGHT SOURCES

By Raymond Davis and Gerald Kent Neeland

ABSTRACT

The variation of photographic sensitivity (as measured by the index $10/E_m$) with different light sources of equal visual intensity, but having different distributions of energy, was experimentally obtained. Ordinary, orthochromatic, and three new fast panchromatic plates were investigated. Distinction was made between two types of sensitivity comparisons. Thus it was found that, first, the ratio of the sensitivity of any one of the panchromatic plates to that of the ordinary plate was greater with "incandescent" lighting than when "sunlight" was used, and second, in all cases the panchromatic plates were less sensitive to "incandescent" lighting than to "sunlight." Approximate factors are included (for the particular emulsions studied) by which visual exposure meter readings should be multiplied when certain types of illuminants are encountered.

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I. INTRODUCTION

The sensitivity of photographic emulsions to various light sources having different spectral energy distributions has recently become of considerable interest. This is due, in part, to the discovery of new dyes which make possible increased sensitivity to the red end of the spectrum.

Artificial illuminants, particularly incandescent lamps, have a relatively large amount of energy in the longer wave lengths. With such illumination, therefore, it is natural to expect the increase in red sensitivity to make the new emulsions more efficient than former ones, i. e., less exposure will be required to obtain the same photographic effect.

Comparisons of sensitivity may be made in one of two ways. First, one may compare the sensitivity of two different emulsions using the same source. Second, the sensitivity of an emulsion to one source may be compared with its sensitivity to another source of equal "intensity" but having a different relative spectral energy distribution.[1]

The question arises as to whether equal "intensity" should be taken to mean equal energy or equal visual intensity. That the two would not be necessarily the same is obvious. In certain problems, such as, for example, determining the type of illuminant which is

[1] The terms "relative spectral energy distribution" and "energy distribution" have the same meaning in this paper.

most efficient with a given emulsion, it is desirable to have the sources under comparison arranged to deliver to the plate the same amount of energy per unit time. With this arrangement, the source to which the emulsion has the higher sensitivity would be the most efficient; that is, a greater photographic effect is obtained with a given amount of energy.

However, in carrying out the experimental work of this paper, we have taken equal intensity to mean equal visual intensity. That this condition for sensitivity comparisons has practical significance may be seen from consideration of a "visual photometer" type of exposure meter in common use. With this instrument the exposure for two objects is indicated as being the same when the light reflected from each object appears equally bright regardless of its energy distribution.[2] Therefore, to use this type of meter properly, it is necessary to know how the sensitivity of the emulsion varies with different types of illuminants.

In this paper are given several examples showing the variation in sensitivity (of panchromatic, orthochromatic, and ordinary plates) with the energy distribution of the light where the visual intensity of the light incident on the emulsion is kept constant. This information is of interest, not only with regard to the use of an exposure meter, but particularly because it furnishes actual data on the performance of new panchromatic emulsions as compared with ordinary emulsions.

II. PROCEDURE AND RESULTS

The emulsio studied were exposed to three sources each having a different energy distribution. These were: (1) an incandescent lamp operating at a color temperature[3] of 2,360° K.; (2) an incandescent lamp operating at a color temperature of 2,810° K.; and (3) an incandescent lamp operating at 2,360° K. in combination with a Davis-Gibson filter such that the resulting light closely approximates the chromaticity and the energy distribution of mean noon sunlight.[4]

Energy distribution curves for these three sources together with the visibility curve, V, are given in Figure 1.

These sources were chosen because it was desired to approximate, as far as possible with available equipment, light conditions, both out of doors in sunlight and inside with incandescent illuminants. Thus the ordinary 60-watt gas filled incandescent lamp approximates a color temperature of 2,800° K. while the old vacuum tungsten lamp approximates a color temperature of 2,400° K. The incandescent lamps, such as are used for studio work in motion pictures, are close to a color temperature of 3,000° K.

The sources were placed in a nonintermittent sectorwheel sensitometer [5] at such distances from the plane of the emulsion that the visual intensity at this plane was 1 meter candle.

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[2] It is assumed here that the photometer employs no blue, or other, "correction" filter. However, the mere inclusion of such a filter would not, necessarily, correct for the different energy distributions of various sources. Thus, only with ordinary plates could reliable readings be obtained with a blue filter.

[3] By a color temperature of 2,360° K. is meant that the chromaticity of the light approximates that of a Planckian radiator at an absolute temperature of 2,360°. In the case of an incandescent lamp, the relative spectral energy distribution, as well as the chromaticity, is also very close to that of the Planckian radiator at the specified temperature.

[4] The chromaticity of mean noon sunlight is approximately that of a Planckian radiator at 5,400° K.

[5] The sensitometer used is described in B. S. Sci. Pap. No. 511.

As pointed out in a previous paper,[6] we believe that the most adequate representation of the sensitivity of an emulsion is given by a curve showing the relation between sensitivity and development time. It was thought best to use the index of sensitivity $10/E_m$[7], where E_m is the exposure value of that point in the "toe" region of the characteristic curve of the emulsion where the gradient is 0.2.

In each test, 24 sensitometric strips, backed with a black shellac mixture to prevent halation, were exposed; 8 to each of the three sources. In several instances the tests were repeated a number of times. The 24 exposed strips were placed in eight racks, each containing three strips, one exposed to each source. The racks were then placed together in a single tray of developer which was kept at 20° C. by a water bath. They were removed, one rack at a time, after periods giving a series of development times from 2 to 22 minutes.

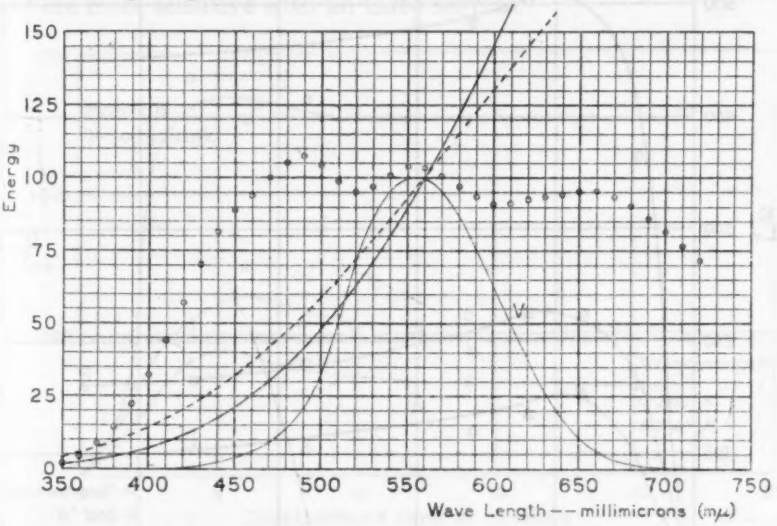

FIGURE 1.—*Relative spectral energy distribution of the light sources used*

The circles represent the spectral energy of the lamp and filter combination producing artificial sunlight. The Eighth International Congress of Photography adopted this as standard for the sensitometry of negative materials. The dashed line represents the spectral energy of 2,810° K. and the solid line 2,360° K., both arbitrarily adjusted to 100 at λ 560 mμ. The visibility curve is marked "V."

Thus the usual range of development times was more than covered. Agitation of the developer was maintained by brushing the plates with a camel's-hair brush.

Pyrogallol-developer, compounded according to the following formula, was employed:

(A)	Water	cc	1, 000
	Potassium metabisulphite	g	12
	Pyrogallol	g	60
(B)	Water	cc	1, 000
	Sodium sulphite (anhydrous)	g	90
(C)	Water	cc	1, 000
	Sodium carbonate (anhydrous)	g	75

[6] For a discussion of several indices and methods of representing sensitivity, see the paper by Raymond Davis and G. K. Neeland, an experimental study of several methods of representing photographic sensitivity, B. S. RP355.

[7] This index was proposed by L. A. Jones in Proc. Seventh Int. Cong. of Phot., 1928, p. 130, and further discussed in the paper by the authors. (See footnote 6.)

To develop, 1 part each of A, B, and C was mixed with 7 parts of water.

The densities of the developed strips were measured in diffuse light with a Martens polarization photometer. A family of eight characteristic curves (total density versus log exposure) was obtained for each source. From each curve a value of the index $10/E_m$ was derived. Thus a measure of the variation of sensitivity with the time of development was obtained for each source. From these data the sensitivity versus development-time curves were drawn.

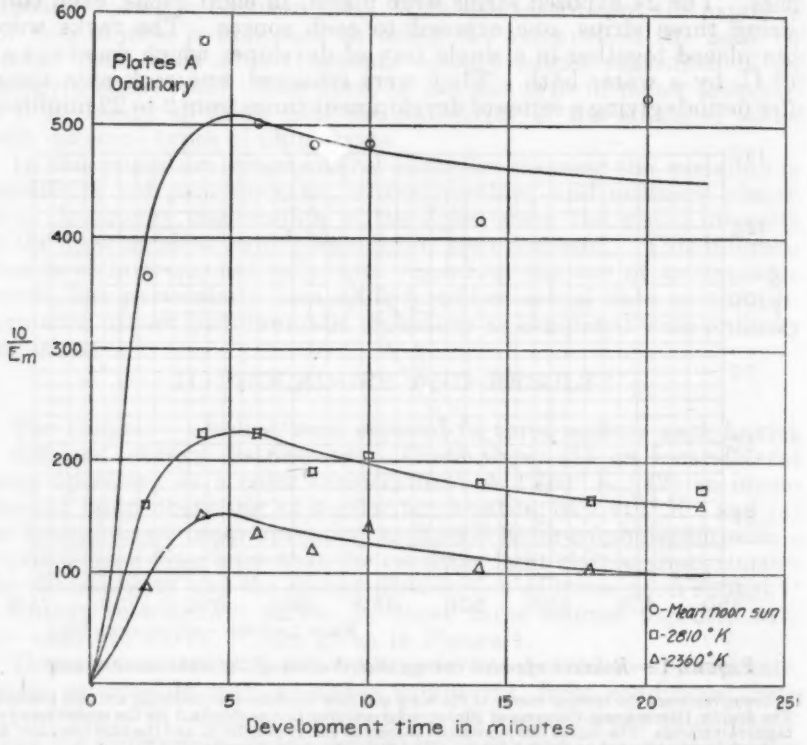

FIGURE 2.—*Sensitivity versus development-time curves for Plates A under three conditions of illumination*

In Table 1 are listed the plates included in the study, the types of emulsions, and the identifying letters used in the figures and tables. The selection is intended to be representative of the most sensitive emulsions now available, and to include an example of each of the three common types of emulsions—ordinary, orthochromatic, and panchromatic.

III. DISCUSSION OF RESULTS

Curves representing the change in sensitivity (as measured by the index $10/E_m$) with the time of development for each of the three sources are given in Figures 2 to 6, inclusive.

In Figure 2 these curves are given for Plates A. The three curves are similar in shape, as would be expected, and show the usual [8]

[8] For a discussion of this type of curve, see the paper by the authors (footnote 6).

optimum time of development (here 5 minutes). Since these plates are "ordinary" (not "color sensitive"), the drop in sensitivity with the lower color-temperature sources is large compared to that for the panchromatic plates.

In Figure 3, similar curves are given for Plates B. Although these plates are orthochromatic the drop in sensitivity is nearly as great as with the ordinary plates.

In Figure 4, the curves for the panchromatic plates (C) indicate a drop in sensitivity which is, for practical purposes, negligible. Although these are not as sensitive as Plates D, their sensitivity is less diminished by the "incandescent" type of illumination.

Figure 5 presents the curves for plates D, the most sensitive of the five brands studied. Even though their loss in sensitivity with "incandescent" illumination is greater than with plates C, the plates D [9] are more sensitive with all three sources.

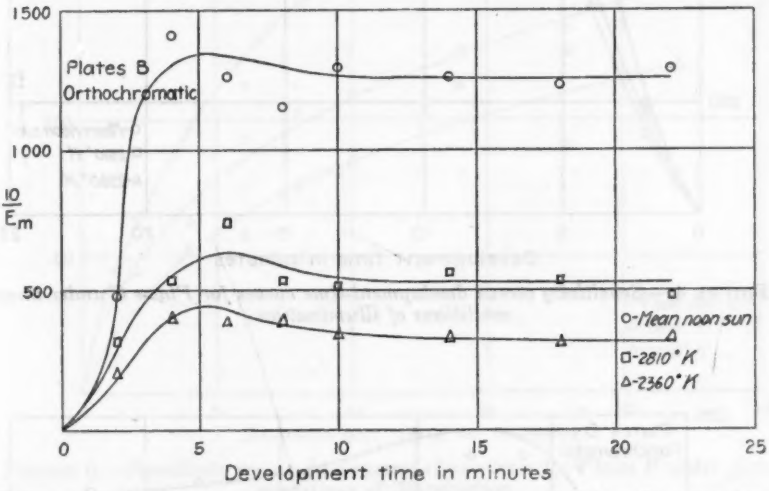

FIGURE 3.—*Sensitivity versus development-time curves for Plates B under three conditions of illumination*

In Figure 6, plates E,[10] we have an example of a panchromatic plate in which the maximum sensitivity is reached at a long time of development.

Table 2 gives the data on the sensitivity (as measured by $10/E_m$) of the five brands of plates in a more easily visualized form. To obtain these values, each sensitivity versus development-time curve is represented by its maximum value.[11] The resulting number is thus more accurately representative than any of the experimentally obtained values of the index. The table shows that (1) the ratio of the sensitivity of the panchromatic to the ordinary plates is greater for "incandescent" lighting than with "sunlight," and (2) with every

[9] It is interesting to note here that these plates, (D), which are advertised to have a higher "H+D" speed to "half-watt" light than to daylight, do not appear to justify the claim.

[10] Although advertised as "special rapid," these plates are considerably slower than the other two brands of panchromatic plates.

[11] The representation of the panchromatic plates E by a single number is not strictly comparable with the others, since the maximum value of the index occurs at a development time exceeding 22 minutes and was therefore unobtainable.

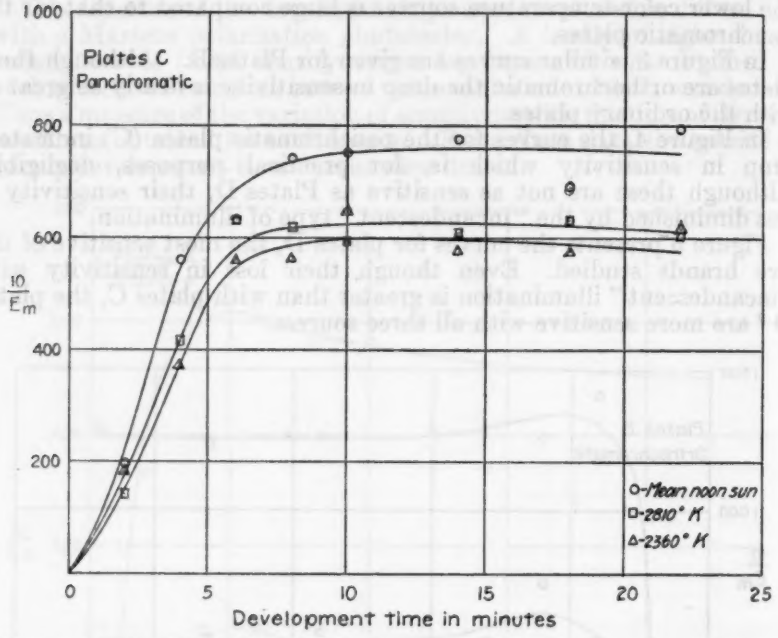

FIGURE 4.—*Sensitivity versus development-time curves for Plates C under three conditions of illumination*

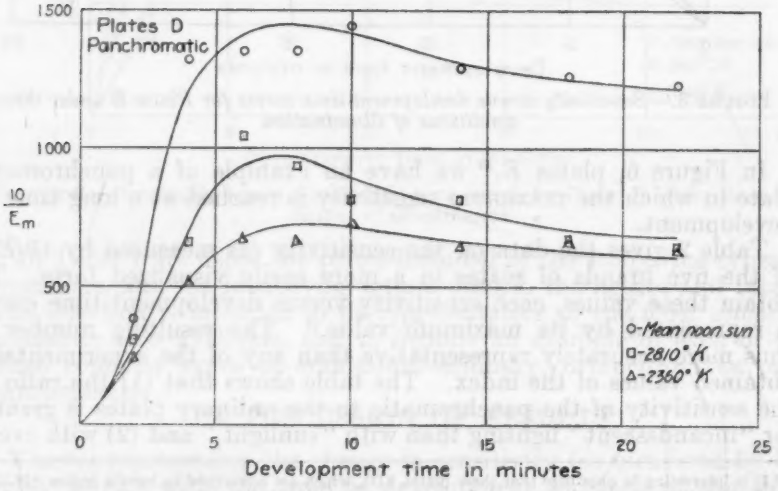

FIGURE 5.—*Sensitivity versus development-time curves for Plates D under three conditions of illumination*

brand of plate the sensitivity decreases with decreasing color temperature of the source.

The values of Table 3 were obtained from the data in Table 2. This table gives the correct exposure for a given plate to a given source, that of the ordinary plates to sunlight being taken as unity.

At present the use of the "visual photometer" type of exposure meter is fairly common. Usually with such a device provision is made for the difference in sensitivity of the several types of photographic materials. However, assuming that the correct exposure to

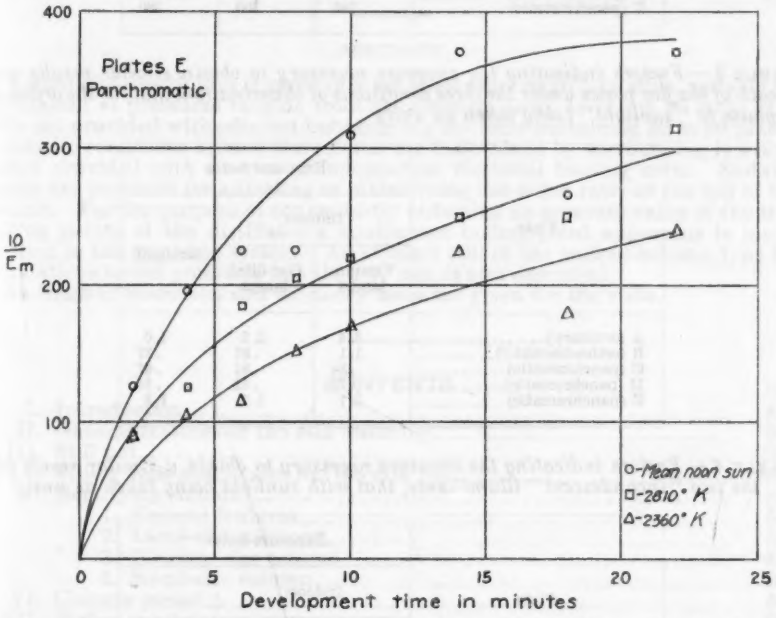

FIGURE 6.—*Sensitivity versus development-time curves for Plates E under three conditions of illumination*

sunlight for a certain brand of plates is known, it is important to know further how the exposure should be modified when using the meter under "incandescent" lighting conditions. This information for the five brands of plates studied is supplied by Table 4.

TABLE 1.—*Photographic plates investigated*

Description of plate	Identification	Figure
American "medium speed" ordinary	A	2
American "high speed" orthochromatic	B	3
American "high speed" panchromatic	C	4
English "high speed" panchromatic	D	5
German "high speed" panchromatic	E	6

TABLE 2.—*Maximum values of $10/E_m$ taken from the sensitivity versus development-time curves*

Plate	Maximum value of the sensitivity index		
	2360° K.	2810° K.	Mean sun
A (ordinary)	150	225	505
B (orthochromatic)	450	620	1,350
C (panchromatic)	600	625	755
D (panchromatic)	725	975	1,450
E (panchromatic)	240	300	380

TABLE 3.—*Factors indicating the exposure necessary to obtain similar results with each of the five plates under the three conditions of illumination, that for the ordinary plates to "sunlight" being taken as unity*

Plate	Exposure factor		
	Indoors		Sunlight
	Vacuum lamps	Gas-filled lamps	
A (ordinary)	3.4	2.2	1.0
B (orthochromatic)	1.1	.81	.37
C (panchromatic)	.84	.81	.67
D (panchromatic)	.70	.52	.35
E (panchromatic)	2.1	1.7	1.3

TABLE 4.—*Factors indicating the exposure necessary to obtain a similar result with the two "incandescent" illuminants, that with sunlight being taken as unity*

Plate	Exposure factor		
	Indoors		Sunlight [1]
	Vacuum lamps	Gas-filled lamps	
A (ordinary)	3.4	2.2	1.0
B (orthochromatic)	3.0	2.2	1.0
C (panchromatic)	1.3	1.2	1.0
D (panchromatic)	2.0	1.5	1.0
E (panchromatic)	1.6	1.3	1.0

[1] These values do not indicate that the plates are equally sensitive to sunlight.

WASHINGTON, September 25, 1931.

LABORATORY RECTIFYING STILLS OF GLASS [1] [2]

By Johannes H. Bruun [3] and Sylvester T. Schicktanz [3]

ABSTRACT

A complete description is given of a set of all-glass rectifying stills, suitable for distillation at pressures ranging from atmospheric down to about 50 mm. The stills are provided with efficient bubbling-cap columns containing 30 to 60 plates. Adiabatic conditions around the column are maintained by surrounding it with a jacket provided with a series of independent electrical heating units. Suitable means are provided for adjusting or maintaining the reflux ratio at the top of the column. For the purpose of conveniently obtaining an accurate value of the true boiling points of the distillates a continuous boiling-point apparatus is incorporated in the receiving system. An efficient still of the packed-column type for distillations under pressures less than 50 mm is also described.

Methods of operation and efficiency tests are given for the stills.

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[1] Presented before the joint session of the divisions of petroleum chemistry, gas and fuel chemistry, and industrial and engineering chemistry at the meeting of the American Chemical Society, Buffalo, N. Y., September 2, 1931.

[2] This paper describes the distillation equipment developed in connection with The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions, listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the central petroleum committee of the National Research Council.

[3] Research associate for the American Petroleum Institute.

I. INTRODUCTION

In order to separate a complex mixture, such as petroleum, as completely and as rapidly as possible by fractional distillation, an efficient equipment is required. The principal requirements and characteristics of such a distillation unit are the following:

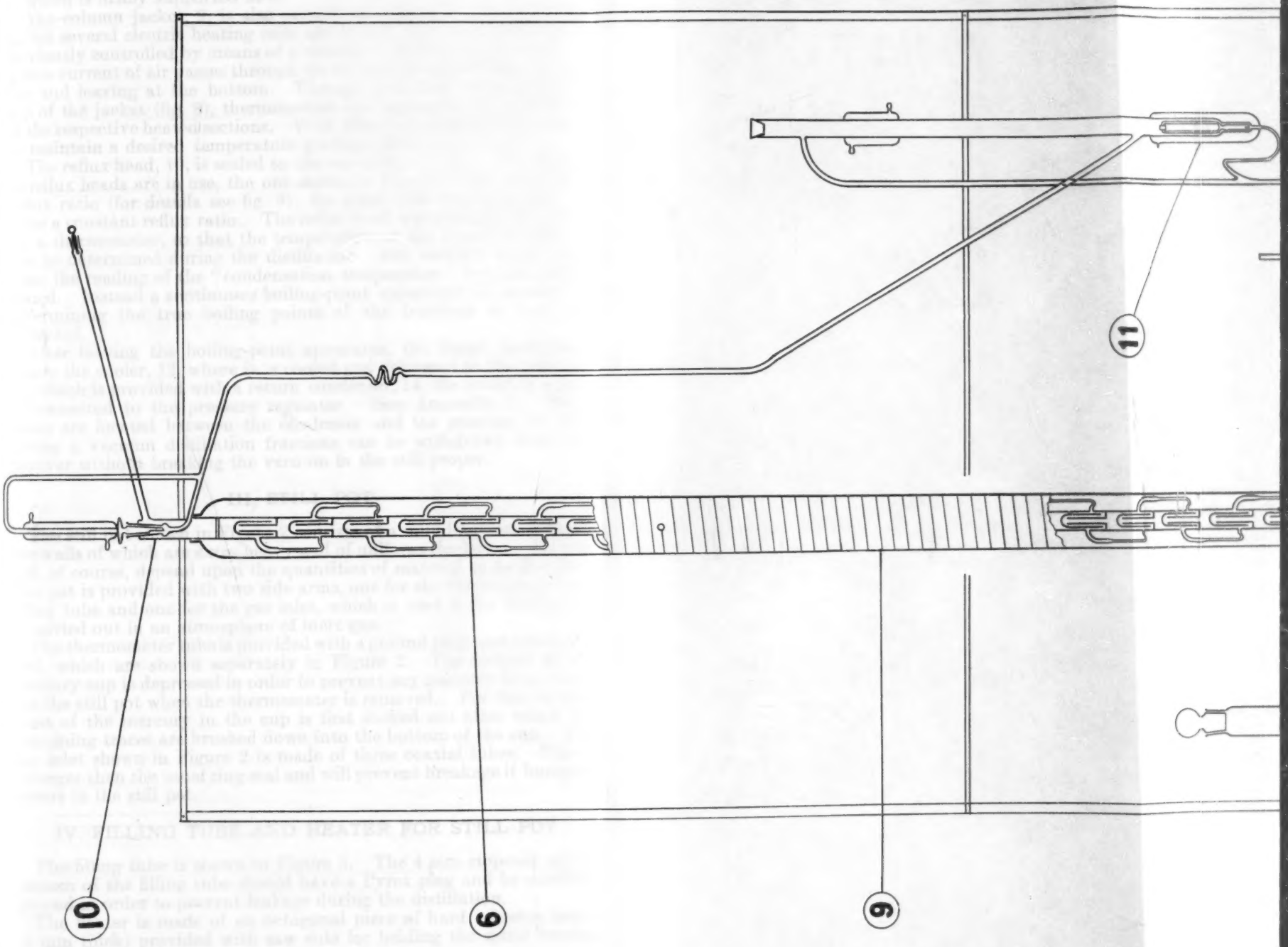
1. An efficient rectifying column. If the over-all vertical distance available is limited, for example, by the height of the laboratory room, the bubble-cap type of column should be employed.
2. Suitable means for adjusting and maintaining the reflux ratio at the top of the column.
3. A device for determining accurately ($\pm 0.05°$ C.) and continuously the true boiling point of the distillate as it is collected, in order that the "cuts" may be properly made.
4. Control of the nature of the atmosphere within the still, in order to prevent oxidation and minimize "cracking."
5. Exact control of the pressure under which the distillation takes place. This is desirable in order to eliminate the influence of variations in barometric pressure which will affect the boiling points of the distillates and thus require the application of corrections before cuts can be correctly made; and in order to permit distillations under reduced pressure when necessary.
6. Provision for exact temperature control of all parts of the system.
7. Provision for withdrawal of distillates without disturbing the operation of the still.
8. Appropriate protection against fire hazard when working with inflammable liquids.

The purpose of this paper is to describe in detail an all-glass still embodying the above characteristics, which has been developed during the past four years, and to give directions for the best operating procedure. While certain features of the still are new and constitute definite improvements over former practice, the general elements of design follow well-known principles. A battery of 10 stills of this type has been operated at the bureau on a continuous 24-hour schedule for the past 15 months with satisfactory results and without a single breakage or accident of any kind.

II. GENERAL FEATURES OF THE STILL ASSEMBLY

An assembly drawing of the still is shown in Figure 1. All parts are constructed of Pyrex laboratory glass. The still pot, 1, is heated by means of an electric heater, 2, which is connected in series with a rheostat. The still pot and its heater are thoroughly insulated from the surroundings by means of a brass container, 3, the inside and top of which are covered with asbestos sheet. This method of heating the still pot has the advantage that in case of an accidental breakage during distillation of inflammable liquids, a fire would be confined principally to the metal container.

The pot is charged through the filling tube, 4. A thermometer is suspended in the still pot through the arm, 5, which is provided with a special mercury seal. The closed side arm on the right is provided for the purpose of attaching a gas inlet, if distillations are to be carried out in an atmosphere of inert gas.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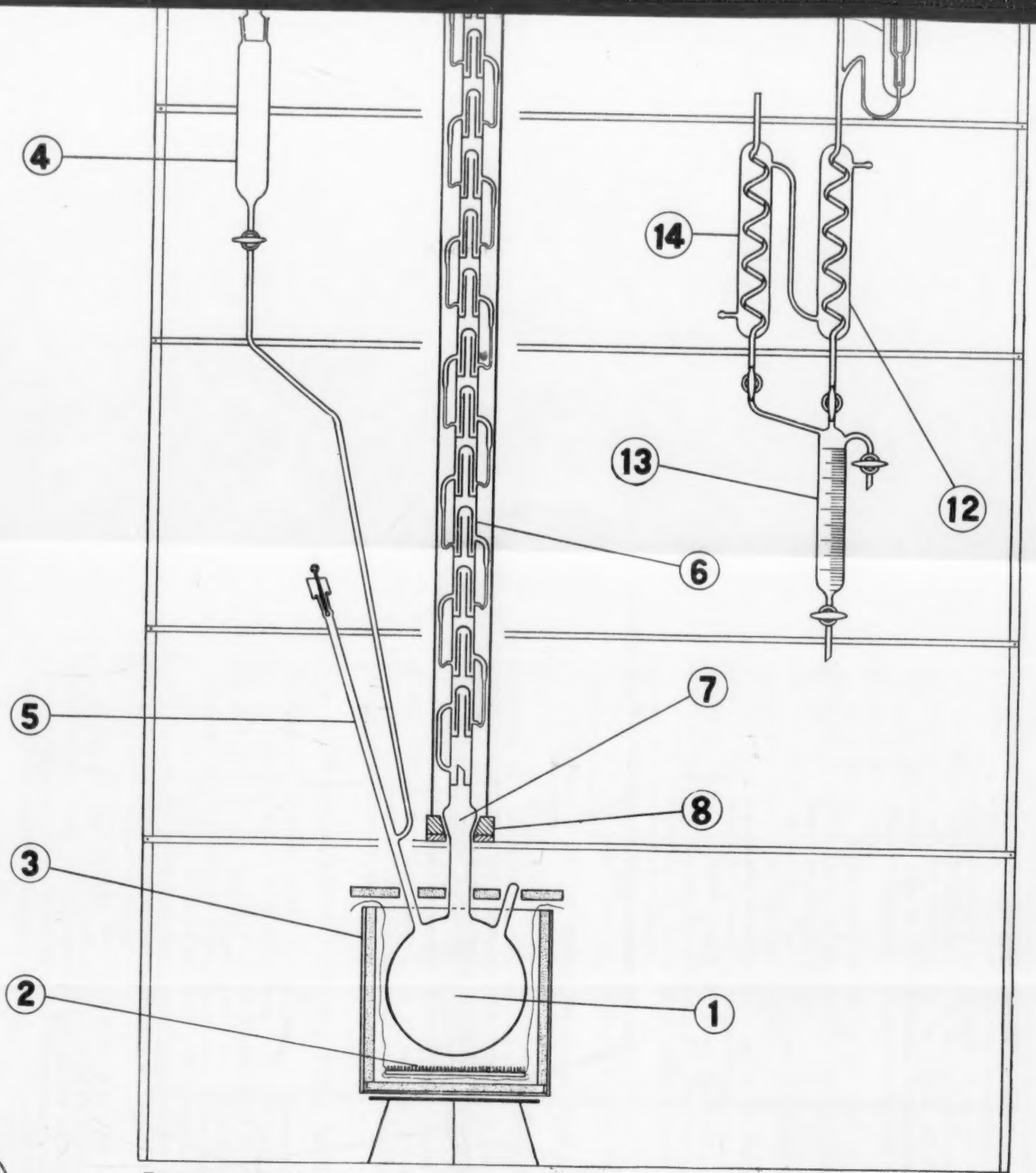


FIGURE 1.—*Assembly of an all glass rectifying still with 30 bubbling-cap plates in the column*

79688—31. (Face p. 852.)

The rectifying column, 6, consists of 30 to 60 bubbling-cap plates. The column is sealed to the still pot by means of a connecting joint, 7, which is firmly supported at 8.

The column jacket, 9, is also carried on support 8. Around this jacket several electric heating coils are wound, each of which is independently controlled by means of a rheostat. During the distillation, a slow current of air passes through the column jacket, entering at the top and leaving at the bottom. Through a vertical opening at the top of the jacket (fig. 8), thermometers are suspended in the centers of the respective heated sections. With this arrangement it is possible to maintain a desired temperature gradient along the column.

The reflux head, 10, is sealed to the top of the column. Two types of reflux heads are in use, the one shown in Figure 1 is for a variable reflux ratio (for details see fig. 9); the other (for details see fig. 10) is for a constant reflux ratio. The reflux head is provided with a tube for a thermometer, so that the temperature at the top of the column can be determined during the distillation. For accurate work, however, the reading of the "condensation temperature" has been abandoned. Instead a continuous boiling-point apparatus, 11, is used for determining the true boiling points of the fractions as they are collected.

After leaving the boiling-point apparatus, the liquid condensate enters the cooler, 12, where it is cooled and delivered to the receiver, 13, which is provided with a return condenser, 14, the outlet of which is connected to the pressure regulator. (See Appendix I.) Stopcocks are located between the condenser and the receiver, so that during a vacuum distillation fractions can be withdrawn from the receiver without breaking the vacuum in the still proper.

III. STILL POT

The still pot shown in Figure 2 consists of a round-bottomed flask, the walls of which are extra heavy and of uniform thickness. Its size will, of course, depend upon the quantities of material to be distilled. The pot is provided with two side arms, one for the thermometer and filling tube and one for the gas inlet, which is used if the distillation is carried out in an atmosphere of inert gas.

The thermometer tube is provided with a ground joint and a mercury seal, which are shown separately in Figure 2. The bottom of the mercury cup is depressed in order to prevent any mercury from entering the still pot when the thermometer is removed. For this purpose most of the mercury in the cup is first sucked out after which the remaining traces are brushed down into the bottom of the cup. The gas inlet shown in Figure 2 is made of three coaxial tubes. This is stronger than the usual ring seal and will prevent breakage if bumping occurs in the still pot.

IV. FILLING TUBE AND HEATER FOR STILL POT

The filling tube is shown in Figure 3. The 4 mm stopcock at the bottom of the filling tube should have a Pyrex plug and be carefully ground in order to prevent leakage during the distillation.

The heater is made of an octagonal piece of hard asbestos board (3 mm thick) provided with saw cuts for holding the spiral heating

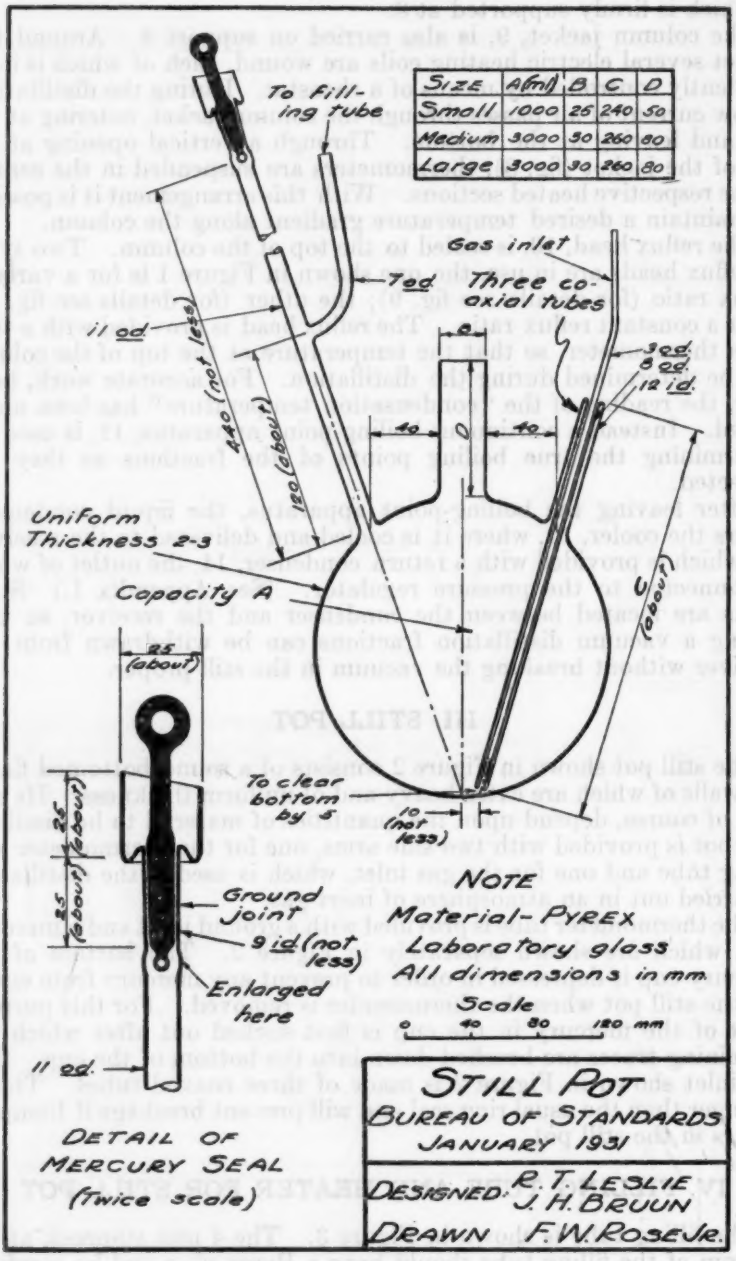


FIGURE 2.—*Still pot*

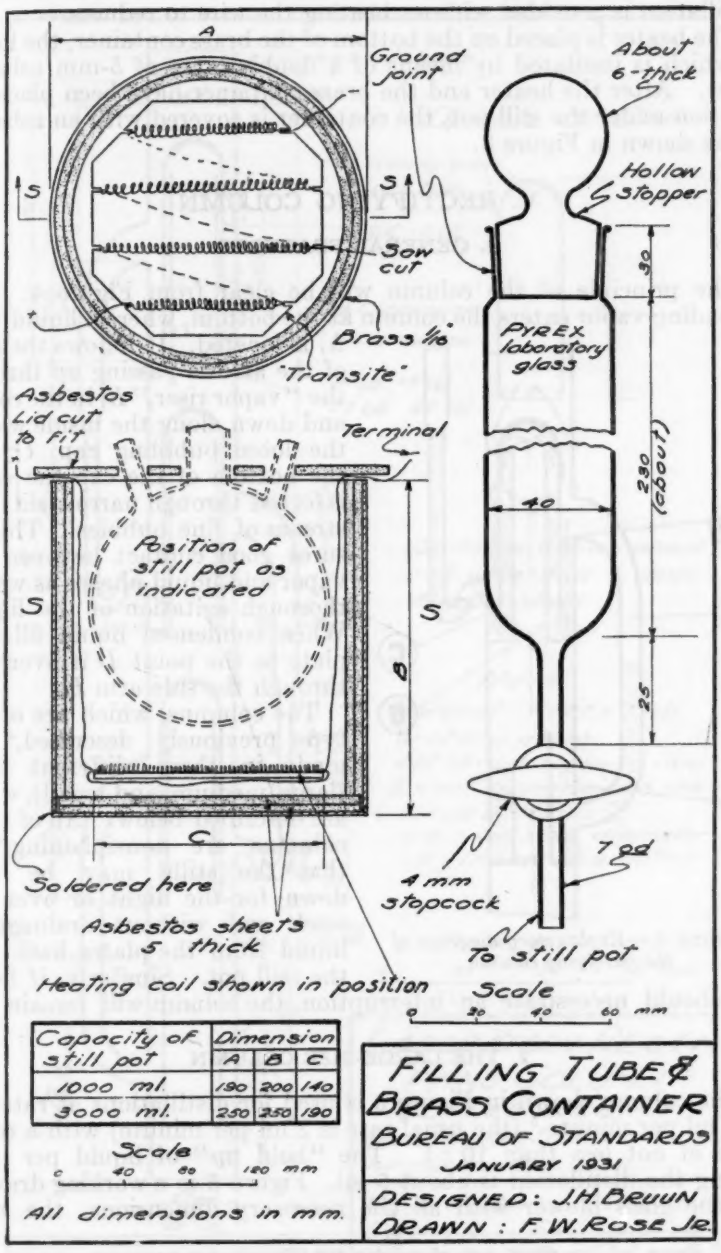


FIGURE 3.—*Filling tube and brass container*

coils. (See fig. 3.) If about 7 of Chromel A heating wire No. 22 is used with a 3-liter pot and a 110-volt circuit, sufficient heat for the distillation is provided without heating the wire to redness.

The heater is placed on the bottom of the brass container, the inside of which is insulated by means of a double layer of 5-mm asbestos sheet. After the heater and the brass container have been placed in position under the still pot, the container is covered with an asbestos lid as shown in Figure 3.

V. RECTIFYING COLUMN

1. GENERAL FEATURES

The principle of the column will be clear from Figure 4. The ascending vapor enters the column at the bottom, where a liquid seal, A, is located. It follows the path of the arrows passing up through the "vapor riser," *B*, in the center and down along the inside wall of the loose bubbling cap, *C*. At the bottom of the cap the vapor is forced through narrow slits in a stream of fine bubbles. This insures good contact between the vapor and liquid phases as well as thorough agitation of the liquid. When condensed liquid fills the plate to the point *D* it overflows through the side arm *E*.

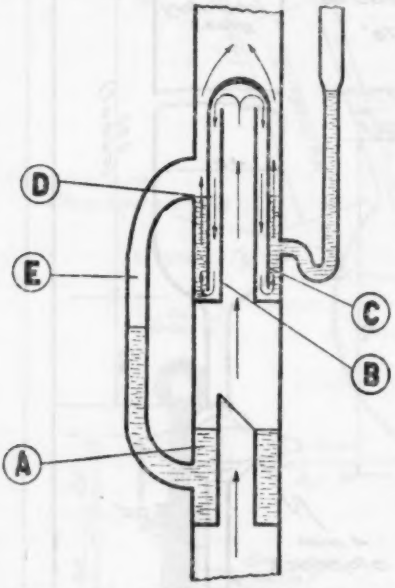


FIGURE 4.—*Explanatory diagram of the rectifying column*

The columns, which are of the type previously described,[4] are made in three different sizes (large, medium, and small), which are described below. All of these columns are nonsiphoning [4] so that the stills may be shut down for the night or over the week end without drainage of liquid from the plates back into the still pot. Similarly, if flooding should necessitate an interruption, the column will remain full.

2. THE LARGE-SIZE COLUMN

The column shown in Figure 5 is used for distillations at rates up to 5 ml per minute [5] (the usual rate is 2 ml per minute) with a reflux ratio of not less than 10 : 1. The "hold up" of liquid per plate during the distillation is about 5 ml. Figure 5 is a working drawing for the glass blower with all the necessary dimensions, the most

[4] J. H. Bruun, Ind. Eng. Chem. Anal. ed., vol. 1, p. 212; 1929.
[5] This, of course, is equivalent to more than 50 ml of liquid per minute returning through the column.

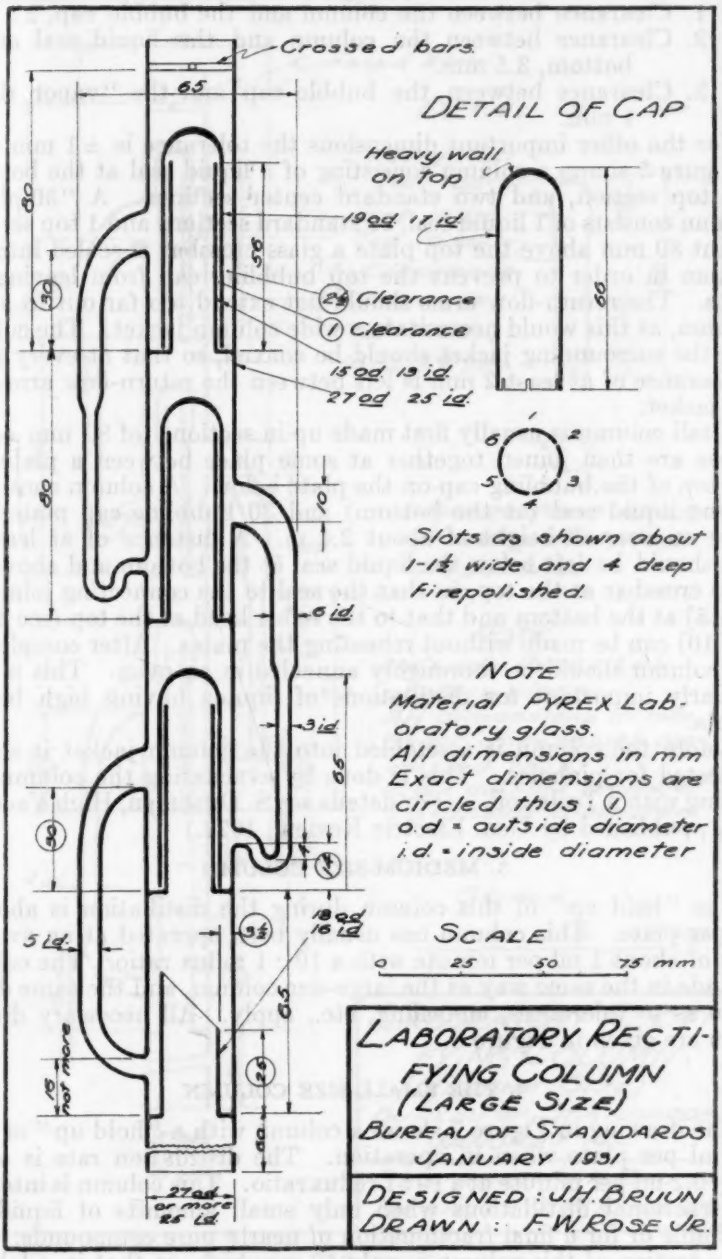


FIGURE 5.—*Large-size column*

important ones being inclosed in circles. The following clearances should be adhered to as closely as possible:

1. Clearance between the column and the bubble cap, 2.5 mm.
2. Clearance between the column and the liquid seal at the bottom, 3.5 mm.
3. Clearance between the bubble cap and the "vapor riser," 1 mm.

For the other important dimensions the tolerance is ±1 mm.

Figure 5 shows a column consisting of a liquid seal at the bottom, one top section, and two standard center sections. A "30-plate" column consists of 1 liquid seal, 29 standard sections and 1 top section. About 80 mm above the top plate a glass crossbar is sealed into the column in order to prevent the top bubbling cap from leaving the plate. The return-flow arms should not extend too far out from the column, as this would necessitate a wide column jacket. The column and the surrounding jacket should be coaxial, so that at every place a clearance of at least 2 mm is left between the return-flow arms and the jacket.

A tall column is usually first made up in sections (of 80 mm each). These are then joined together at some place between a plate and the top of the bubbling cap on the plate below. A column consisting of one liquid seal (at the bottom) and 30 bubbling-cap plates will have an over-all height of about 2.4 m. A distance of at least 60 mm should be left below the liquid seal at the bottom and above the glass crossbar at the top, so that the seal to the connecting joint (see fig. 15) at the bottom and that to the reflux head at the top (see figs. 9 and 10) can be made without reheating the plates. After completion, the column should be thoroughly annealed in an oven. This is particularly important for distillations of liquids having high boiling points.

Before the column is assembled into the column jacket it should be tested for pinholes. This is done by evacuating the column and testing with a Tesla coil. (For details see S. Dushman, High Vacuum, p. 81, published by Gen. Electric Review; 1922.)

3. MEDIUM-SIZE COLUMN

The "hold up" of this column during the distillation is about 4 ml per plate. This column has usually been operated at an average rate of about 1 ml per minute with a 10 : 1 reflux ratio. The column is made in the same way as the large-size column, and the same directions as to tolerances, annealing, etc., apply. All necessary dimensions are given in Figure 6.

4. THE SMALL-SIZE COLUMN

The drawing in Figure 7 shows a column with a "hold up" of only 0.6 ml per plate when in operation. The distillation rate is about 0.1 − 0.2 ml per minute at a 10 : 1 reflux ratio. This column is intended for fractional distillations when only small amounts of liquid are available or for a final fractionation of nearly pure compounds. One plate section of this column is only 40 mm high, so that in a laboratory of average height (about 3.5 m) it is possible to mount a rectifying column containing about 60 plates. All necessary dimensions for the small column are given on the drawing. The general specifications given for the large column also apply to this one.

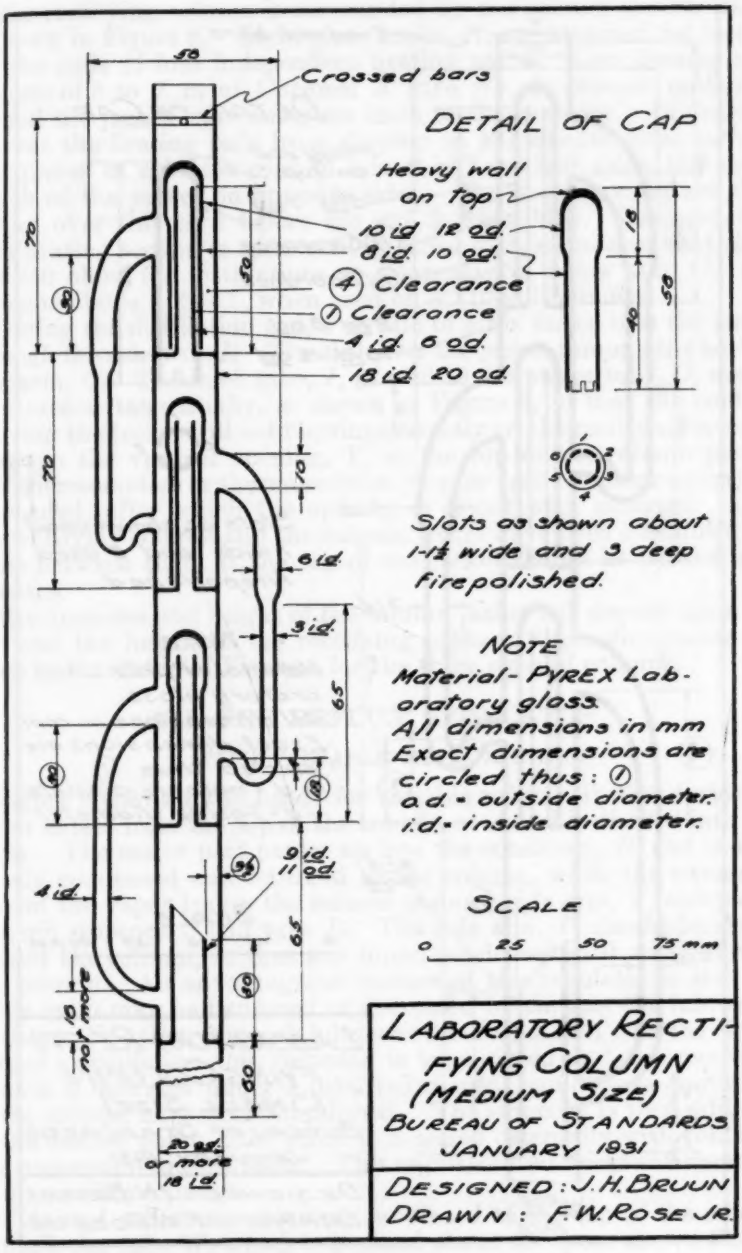


FIGURE 6.—*Medium-size column*

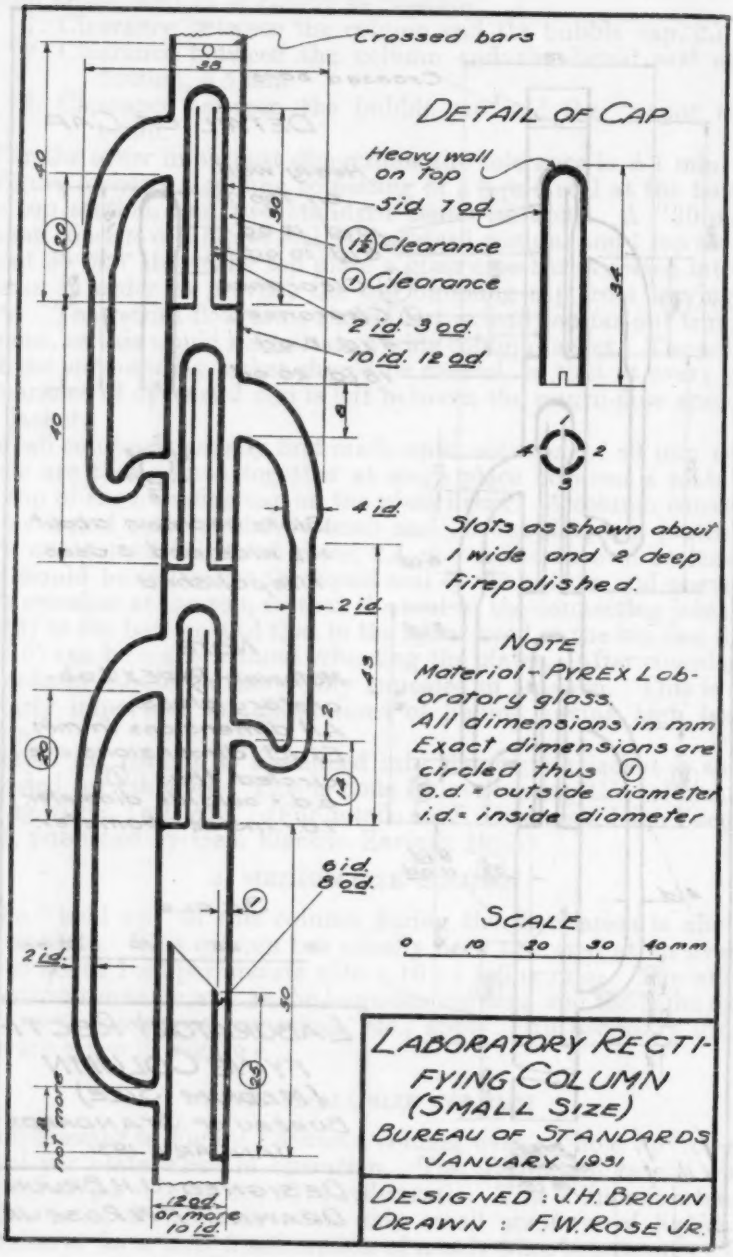


FIGURE 7.—*Small-size column*

VI. THE COLUMN JACKET

The rectifying column is surrounded by the column jacket, which is shown in Figure 8. Eight glass knobs, *K*, are attached for fastening the ends of four independent heating units. Each heating unit consists of 6 to 7 m of Chromel A wire No. 22 wound uniformly around the jacket from one glass knob to the next one. In order to prevent the heating coils from slipping on the smooth glass surface, two pieces of asbestos cord (6 mm thick) are laid along the entire length of the jacket on opposite sides. The heating wires are then wound over this cord before the still is assembled. For operation each heating section is connected in series with an independent rheostat (50 ohms for distillations at temperatures below 100° C., and 16 ohms above 100° C., when used on a 110-volt circuit).

During the distillation a slow stream of air is forced into the jacket through the side arm, *I*. The air leaves the jacket through the bottom side arm, *O*. The inlet tube, *I*, as well as the outlet tube, *O*, should be attached tangentially, as shown in Figure 8, so that the cold air entering the jacket will not impringe directly on the rectifying column. Through the vertical opening, T, at the top of the column jacket, four thermometers or thermocouples (one for each heating section) are suspended, after which the opening is closed with asbestos. After the rectifying column and the column jacket have been assembled the space between them at the top of the jacket should be packed with asbestos.

The diameter and height of the column jacket will depend upon the size and the height of the rectifying column; these dimensions are given in the Table of Figure 8 for the three sizes of column.

VII. THE REFLUX REGULATOR

1. WITH VARIABLE REFLUX RATIO

Figure 9 shows a still head [6] for variable reflux. In this device the vapor enters from the top of the column at *A* and is divided into two parts. The major part passes up into the condenser, *B*, and is completely condensed and returned to the column, while the remaining part of the vapor leaves the column through side arm, *T*, and passes through stopcock *S* and tube *L*. The side arm, *T*, should be sloped toward the column, so that any liquid condensed in it will return to the column. An advantageous feature of this regulator is that the reflux ratio may be increased or decreased by turning the lubricated stopcock, *S*. (For stopcock lubricant see Sec. XIV.) In the beginning of a distillation this stopcock is kept closed and the rectifying column is operated under a total reflux until equilibrium conditions in the column have been established. The stopcock is then adjusted to the desired point, after which it is sealed externally with collodion as a precaution against leaks. This regulator also works satisfactorily for immiscible liquids.

If desired a thermometer may be placed at the top of the column through the tube W, which is inclined about 60° from the vertical in order to allow more height for the column. This tube is provided with a ground joint at the top.

[6] A reflux head of a somewhat similar design has been described by M. J. Marshall, Ind. Eng. Chem., vol. 20, p. 1379; 1928.

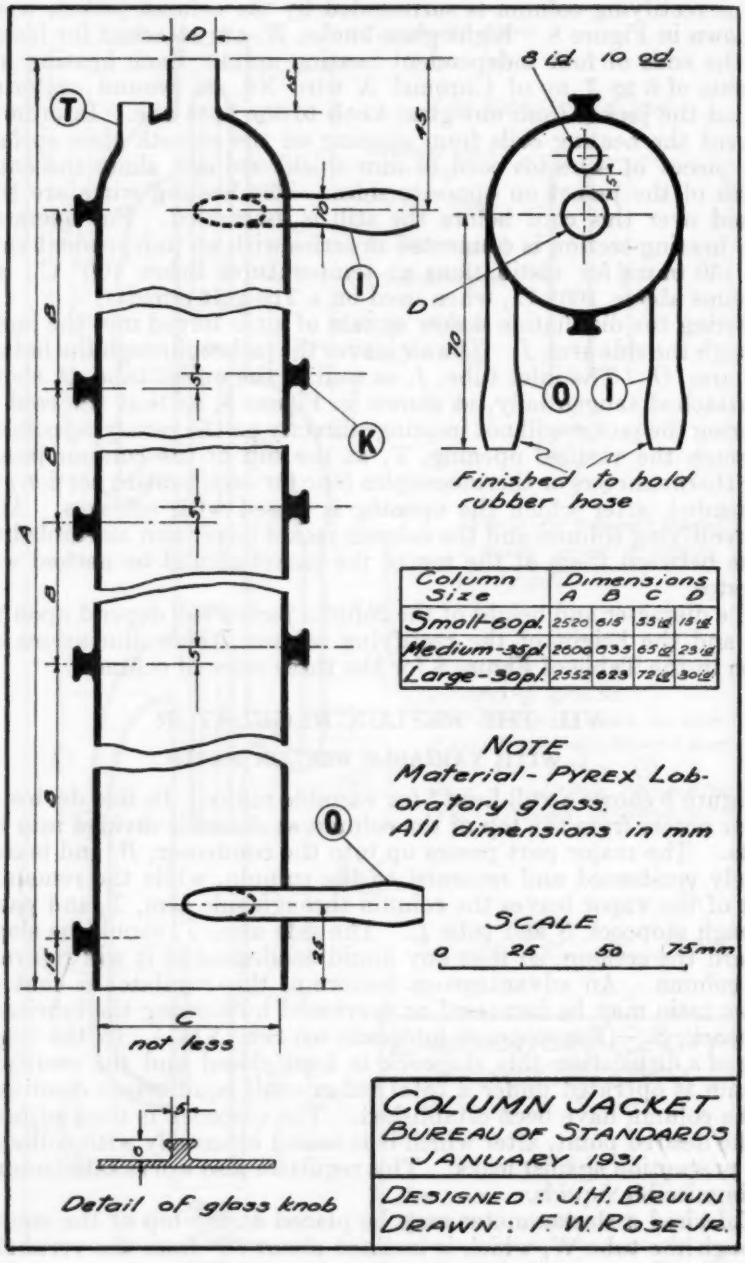


FIGURE 8.—*Column jacket*

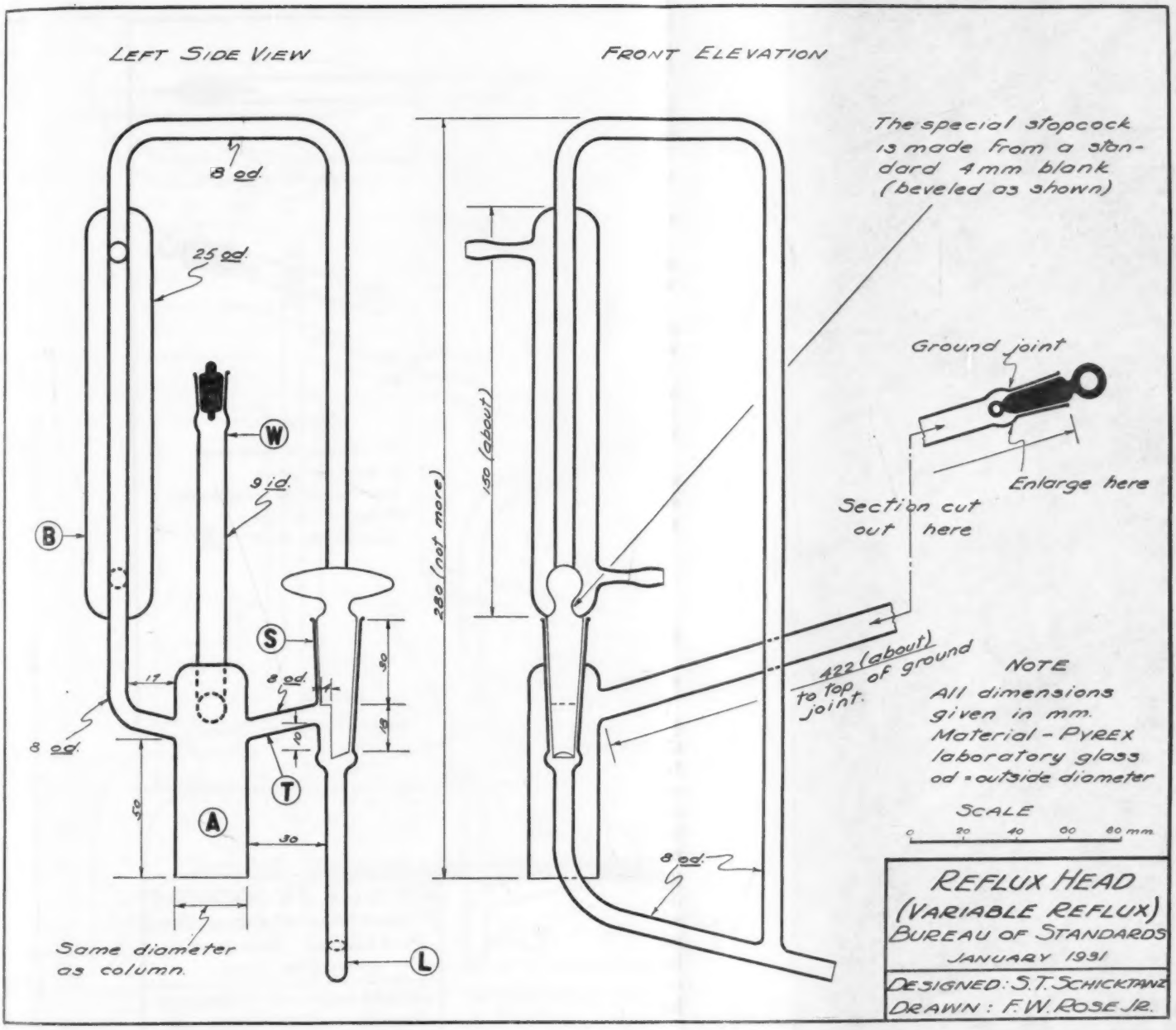


FIGURE 9.—*Reflux regulator for variable reflux ratio*

79688—31. (Face p. 862.) No. 1

W
S
T
A
L

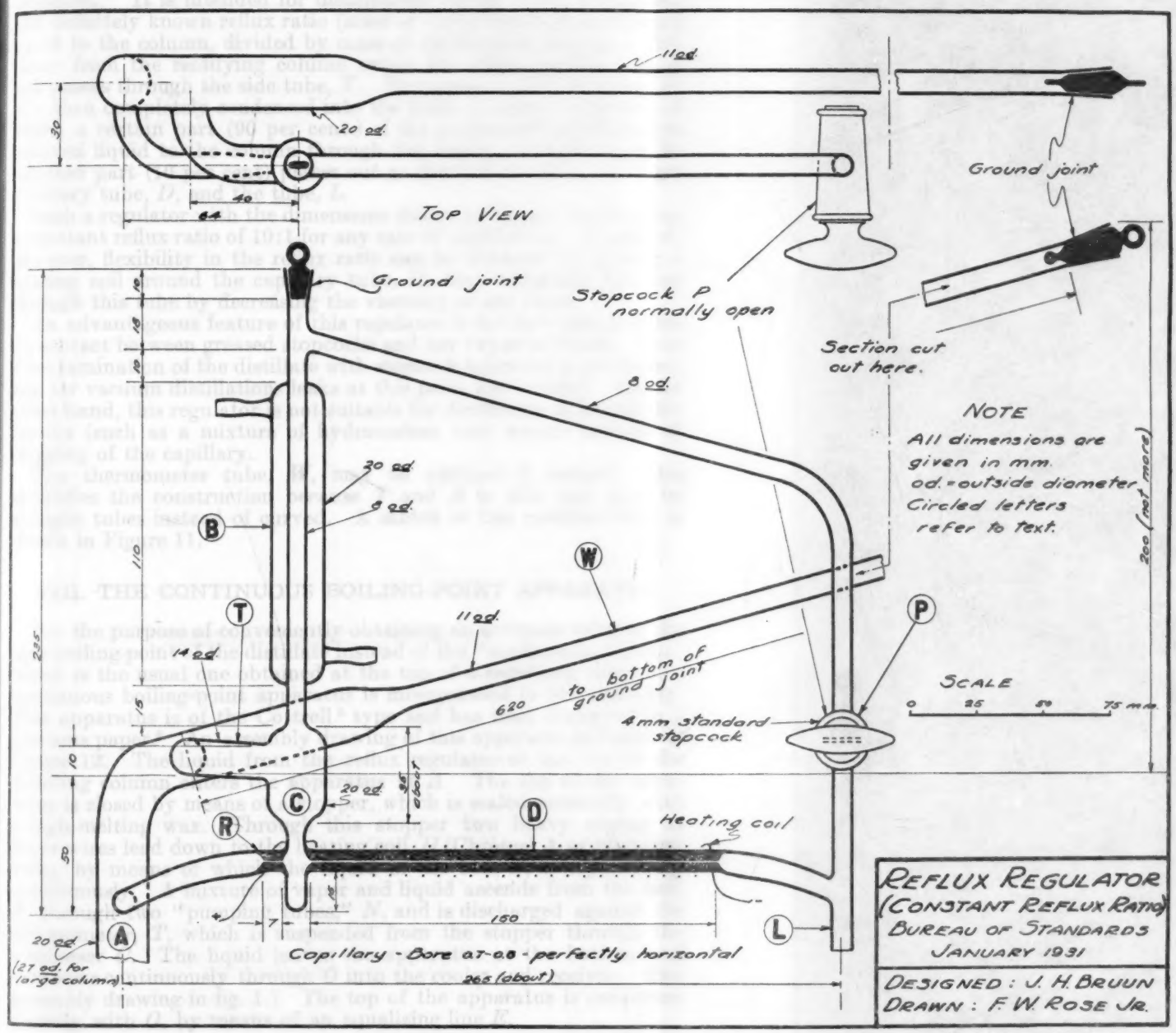
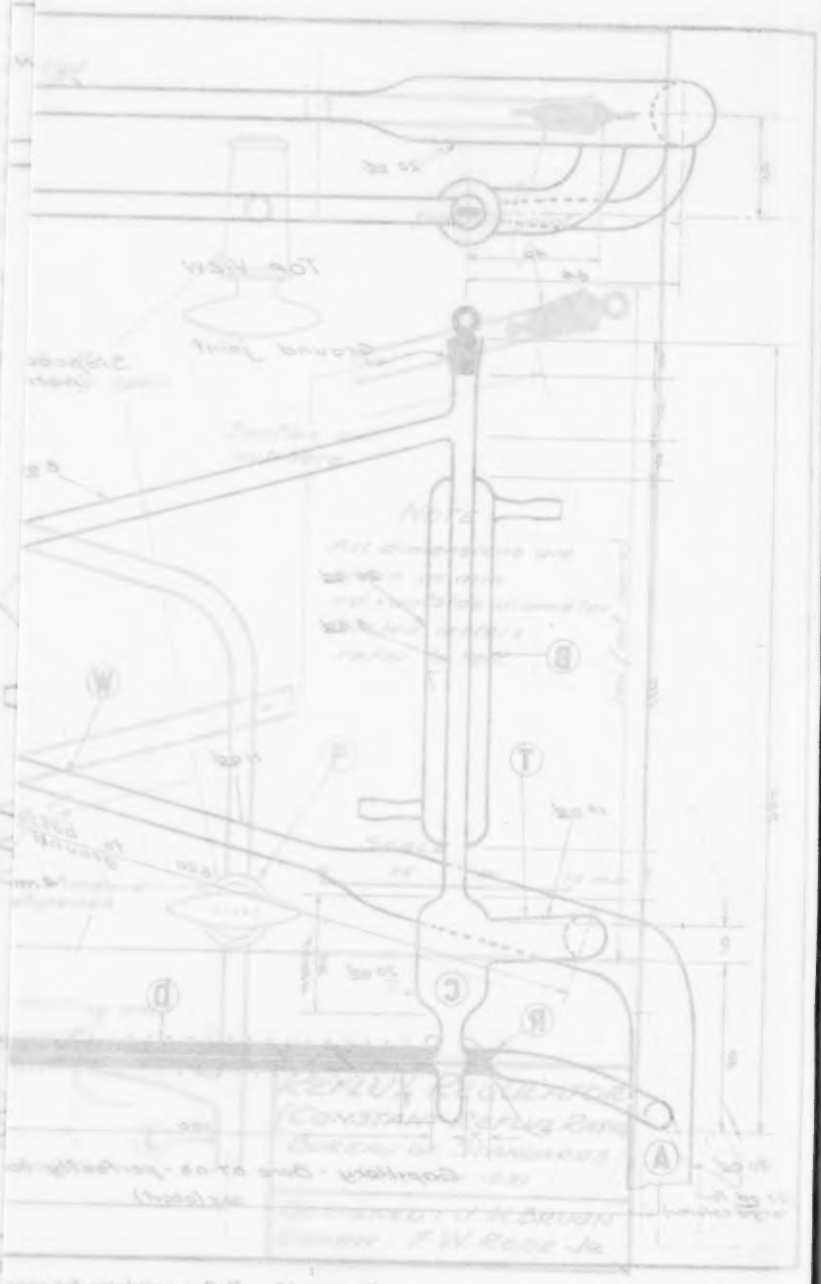


FIGURE 10.—*Reflux regulator for constant (10 : 1) reflux ratio*


W
D
T
C
R
A

2. WITH CONSTANT REFLUX RATIO

Figure 10 shows a working drawing of a reflux regulator previously described.[7] It is intended for distillations during which a constant and definitely known reflux ratio (mass of vapor returned as refluxed liquid to the column, divided by mass of distillate) is desired. The vapor from the rectifying column enters the reflux regulator at *A* and passes through the side tube, *T*. By means of the condenser, *B*, it is then completely condensed into the bulb, *C*, from the bottom of which a certain part (90 per cent.) of the condensate is returned as refluxed liquid to the column through the shorter capillary tube, *R*. Another part (10 per cent) passes out as distillate through the longer capillary tube, *D*, and the tube, *L*.

Such a regulator with the dimensions shown in Figure 10 maintains a constant reflux ratio of 10:1 for any rate of distillation. If desired, however, flexibility in the reflux ratio can be obtained by placing a heating coil around the capillary tube, *D*, thus increasing the flow through this tube by decreasing the viscosity of the liquid.

An advantageous feature of this regulator is the fact that it offers no contact between greased stopcocks and hot vapor or liquid. Thus a contamination of the distillate with stopcock lubricant is prevented, and for vacuum distillations leaks at this point are avoided. On the other hand, this regulator is not suitable for distillation of immiscible liquids (such as a mixture of hydrocarbon with water) because of clogging of the capillary.

The thermometer tube, *W*, may be omitted if desired. This simplifies the construction because *T* and *R* in this case may be straight tubes instead of curved. A sketch of this modified form is shown in Figure 11.

VIII. THE CONTINUOUS BOILING-POINT APPARATUS

For the purpose of conveniently obtaining an accurate value of the true boiling point of the distillate instead of the "condensation point" which is the usual one obtained at the top of a rectifying column, a continuous boiling-point apparatus is incorporated in the assembly. This apparatus is of the Cottrell[8] type and has been described in a previous paper.[9] An assembly drawing of this apparatus is shown in Figure 12. The liquid from the reflux regulator at the top of the distilling column enters the apparatus at *A*. The top of the apparatus is closed by means of a stopper, which is sealed externally with a high-melting wax. Through this stopper two heavy copper or silver wires lead down to the heating coil, *H* (Chromel A or platinum wire), by means of which the liquid in the bell, *B*, is kept boiling continuously. A mixture of vapor and liquid ascends from the bell, *B*, through two "pumping tubes," *N*, and is discharged against the thermometer, *T*, which is suspended from the stopper through the condenser *C*. The liquid leaves the apparatus at the bottom and overflows continuously through *O* into the cooler and receiver. (See assembly drawing in fig. 1.) The top of the apparatus is connected directly with *O*, by means of an equalizing line *E*.

[7] J. H. Bruun, Ind. Eng. Chem., Anal. Ed., vol. 2, p. 187; 1930.
[8] F. G. Cottrell, J. Am. Chem. Soc., vol. 41, p. 721; 1919.
[9] J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 6, p. 871; 1931.

A 4 mm stopcock may be sealed into the equalizing line, *E*, in order to facilitate the removal of the liquid from the apparatus by suction applied at *O*. The lower part of the apparatus is surrounded by a vacuum jacket, *V*, which should extend well above the top of the pumping tubes, *N*.

A working drawing of the apparatus with all the necessary dimensions is shown in Figure 13. It should be noted that the height of the pumping tubes (*N* in fig. 12) is given as 110 mm in Figure 13. This height has been found to be sufficient for the lower boiling

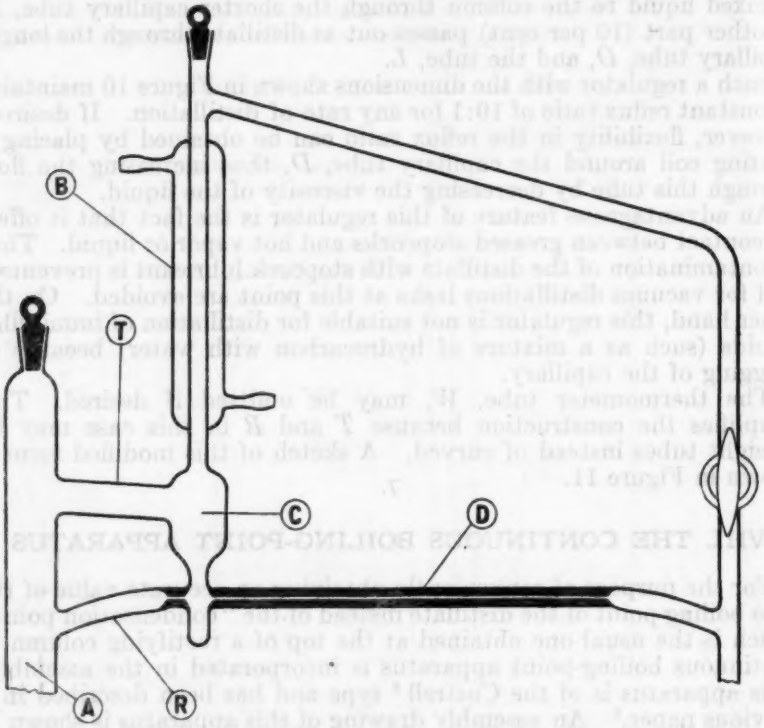


FIGURE 11.—*Reflux regulator for constant reflux ratio. (Without the thermometer tube)*

petroleum fractions, but should probably be increased for more viscous liquids, in order to dissipate superheat.[10]

A more elaborate construction of this apparatus is to replace the stopper at the top of the apparatus with a ground-glass joint provided with two tungsten leads. An improved modification of this type has been used on one rectifying still. For most purposes, however, it was not considered necessary to go to the extra expense of using the ground-joint top. For this reason the simplified form of construction is shown in the figure.

[10] On this point see further, Washburn and Read, J. Am. Chem. Soc. vol. 41, p. 731, par. 1; 1919.

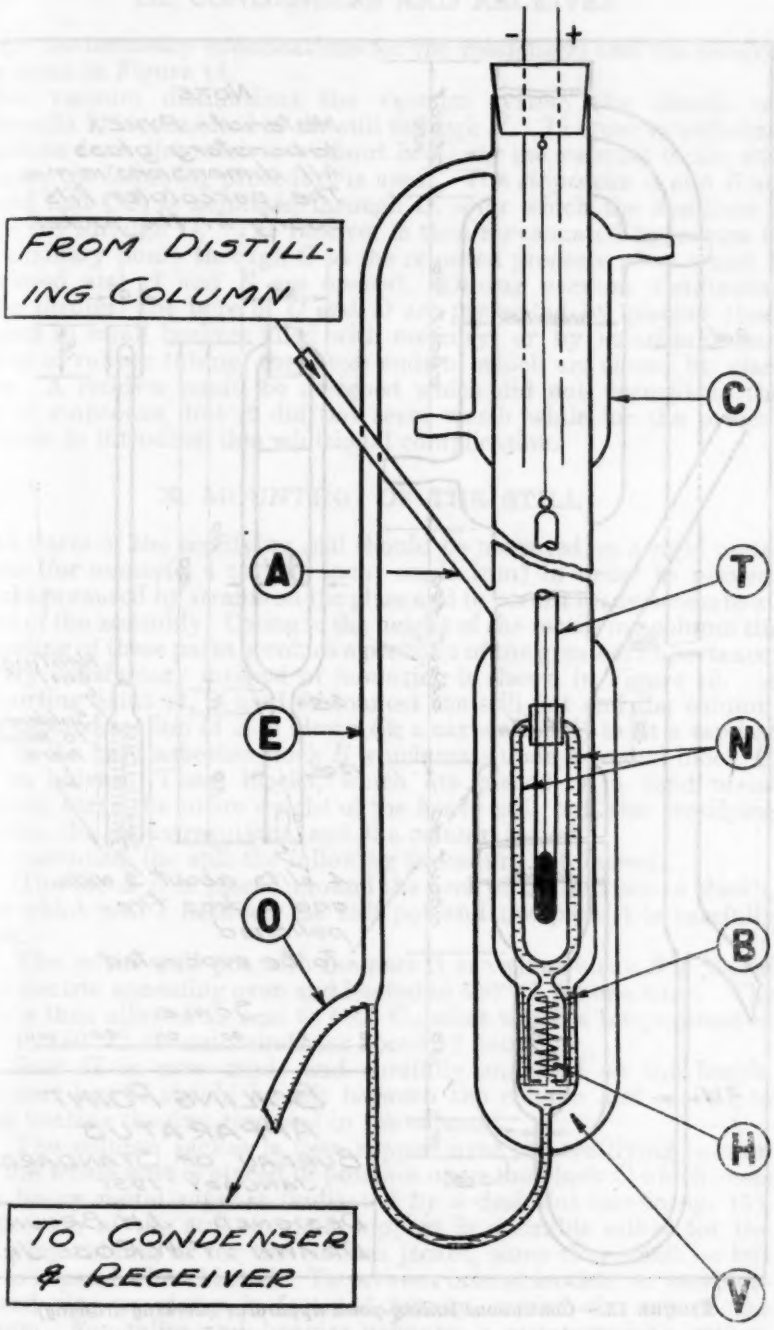


FIGURE 12.—*Continuous boiling-point apparatus (explanatory diagram)*

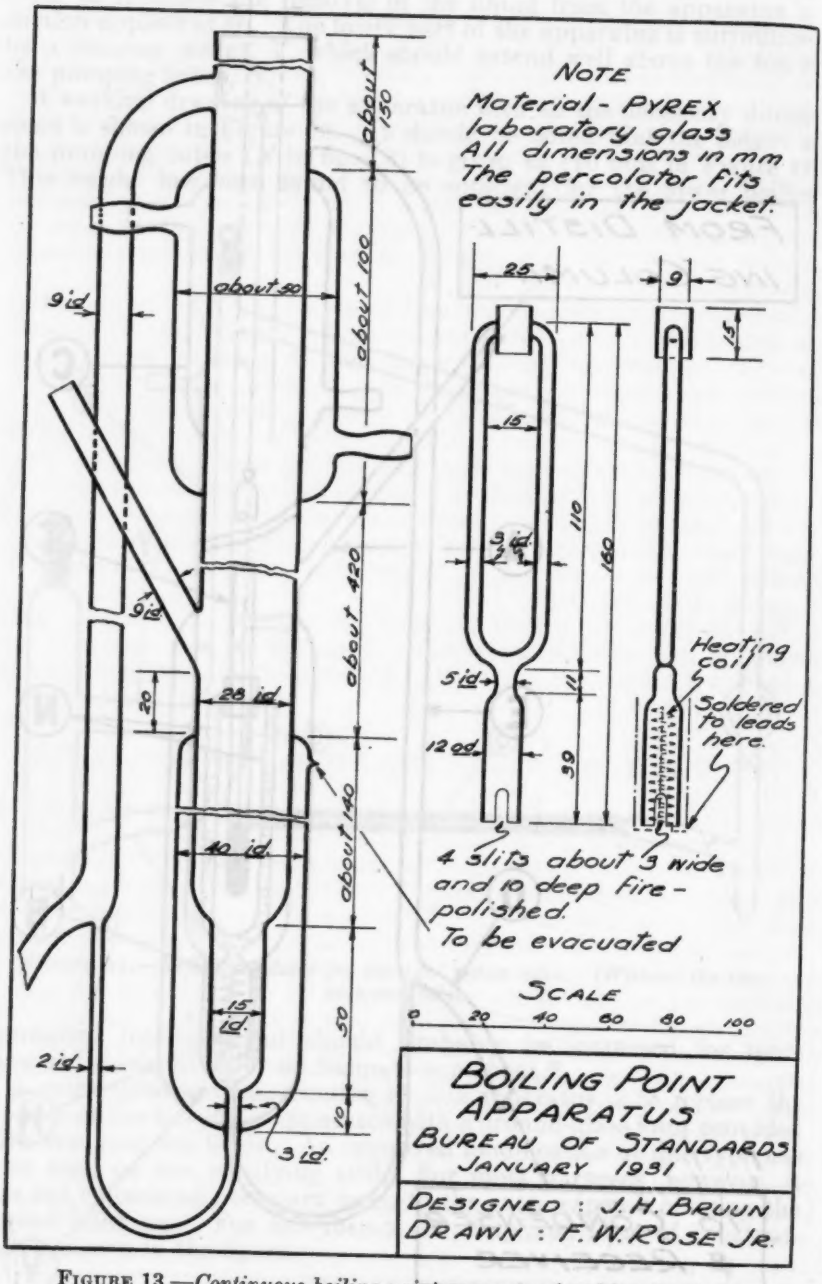


FIGURE 13.—*Continuous boiling-point apparatus (working drawing)*

IX. CONDENSERS AND RECEIVER

All the necessary specifications for the condensers and the receiver are given in Figure 14.

For vacuum distillations the vacuum system (for details see Appendix I) is connected to the still through *V*. In order to withdraw fractions from the receiver without breaking the vacuum in the still proper, the following procedure is used. The stopcocks *A* and *B* are closed and CO_2 is admitted through *C*, after which the distillate is removed through *D*. The receiver is then reevacuated by means of an auxiliary pump through *C* to the required pressure after which *C* is closed and *A* and *B* are opened. During vacuum distillations leaks through the bore of *C* and *D* are prevented by placing these outlets in small beakers filled with mercury, or by attaching short pieces of rubber tubing, the lower ends of which are closed by glass rods. A receiver could be designed which did not necessitate the use of stopcocks, but it did not seem worth while for the present purpose to introduce this additional complication.

X. MOUNTING OF THE STILL

All parts of the rectifying still should be mounted on a rigid metal frame (for example, 4 cm (1½ inch) angle iron) in order to prevent breakage caused by strains on the glass and to permit ready access to all parts of the assembly. Owing to the height of the rectifying column the mounting of these parts becomes a problem of the greatest importance. A very satisfactory method of mounting is shown in Figure 15. A supporting joint *A*, is used to connect the still pot and the column. The tapered section of *A* is blown (in a carbon mold) to fit a tapered hole in the hard asbestos block *B* which rests upon a second block *C*, cut in halves. These blocks, which are placed on a rigid metal support, carry the entire weight of the heavy still pot, the rectifying column, the reflux regulator, and the column jacket.

In mounting the still the following procedure is followed:

1. The block *B* is placed around the neck of the still pot as shown, after which seal I between the still pot and the part *A* is carefully made.

2. The entire still pot with the part *A* as well as block *B* is placed in an electric annealing oven and heated to 550° C. for one hour. The oven is then allowed to cool to 450° C., after which a temperature of 400° to 450° C. is maintained for about 12 hours.

3. Seal II is now made and carefully annealed on the bench. Sufficient length should be left between the column and seal II to avoid heating the first ring seal in the column.

4. The column jacket is then slipped over the rectifying column and the whole unit is placed in position upon the block *C* which rests on a heavy metal support (indicated by a dash-dot line in fig. 15). At the top of the still no rigid support is desirable either for the rectifying column or for the column jacket, since they must be left free to expand when heated. To prevent lateral motion, an asbestos-covered ring or clamp is fastened loosely around the top of the column. For taller and heavier columns a counterweight system should be employed. (See Sec. XIII.)

Figure 16 is a photograph of five of these stills mounted on a single frame.

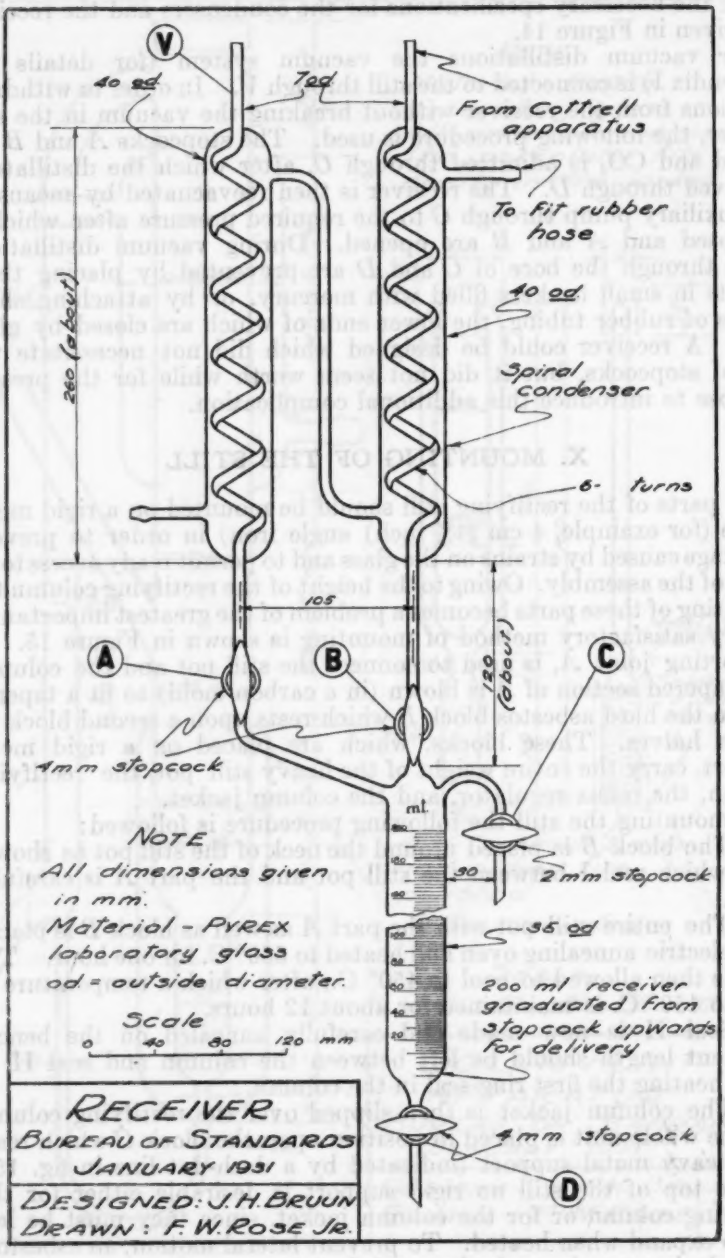
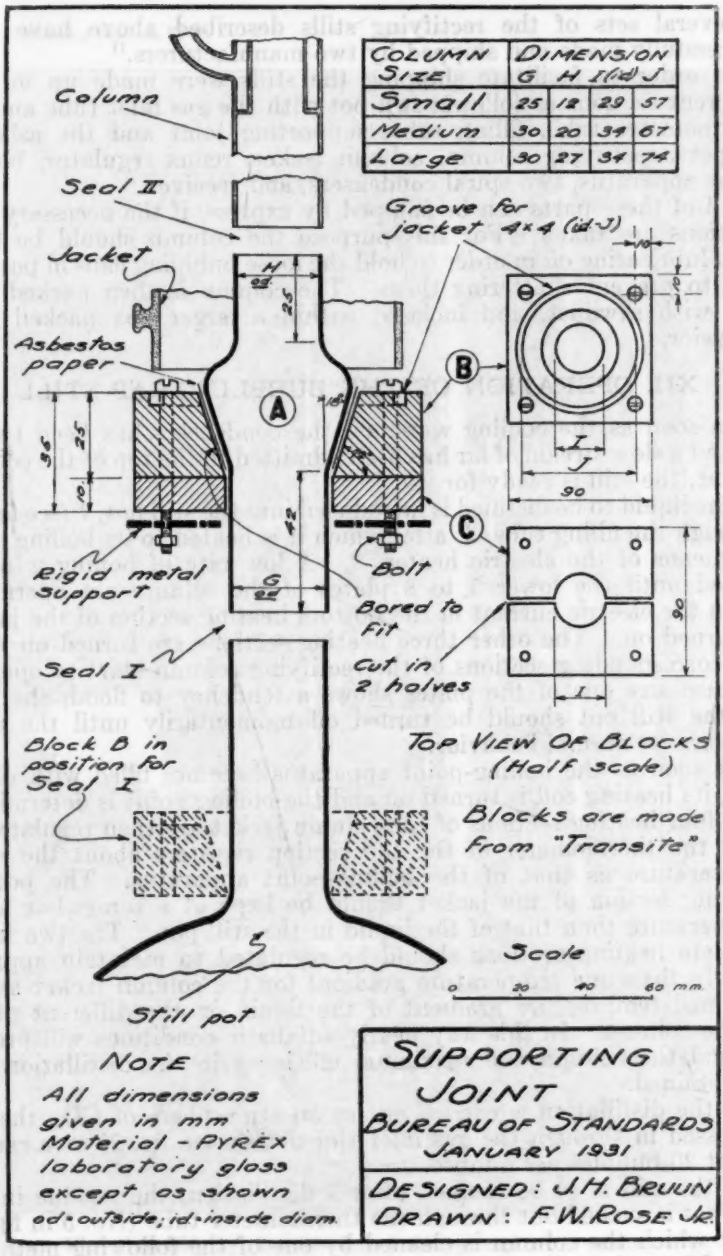


FIGURE 14.—*Receiver and condensers*



COLUMN SIZE	DIMENSION G	H	I (id)	J
Small	25	12	29	57
Medium	30	20	34	67
Large	30	27	34	74

FIGURE 15.—*Method used for supporting the column and the column jacket*

XI. MANUFACTURE AND TRANSPORTATION OF THE BUBBLING-CAP STILLS

Several sets of the rectifying stills described above have been successfully made and shipped by two manufacturers.[11]

In order to facilitate shipping the stills were made up in nine different sections as follows: still pot with the gas inlet tube and the thermometer tube, filling tube, supporting joint and the asbestos support, rectifying column, column jacket, reflux regulator, boiling point apparatus, two spiral condensers, and receiver.

All of these parts can be shipped by express, if the necessary precautions are taken. For this purpose the column should be filled with lubricating oil in order to hold the loose bubbling caps in position and to prevent shattering them. The column is then packed in a box with sawdust, and inclosed within a larger box packed with excelsior.

XII. OPERATION OF THE BUBBLING-CAP STILL

As soon as the cooling water on the condensers has been turned on and a slow stream of air has been admitted to the top of the column jacket, the still is ready for use.

The liquid to be distilled is introduced into the still pot, *1* (see fig. 1), through the filling tube, *4*, after which it is heated to its boiling point by means of the electric heater, *2*. A low rate of boiling is maintained until the lower 5 to 8 plates of the column are operating. Then the electric current in the bottom heating section of the jacket is turned on. The other three heating sections are turned on when the corresponding sections of the rectifying column start to operate. In case any one of the plates shows a tendency to flood, the heat on the still pot should be turned off momentarily until the plate resumes its normal behavior.

As soon as the boiling-point apparatus becomes filled with distillate, its heating coil is turned on and the boiling point is determined. The four heating sections of the column jacket are then regulated so that the thermometer of the top section registers about the same temperature as that of the boiling-point apparatus. The bottom heating section of the jacket should be kept at a somewhat lower temperature than that of the liquid in the still pot. The two intermediate heating sections should be regulated to maintain approximately the same temperature gradient for the column jacket as the assumed tempreature gradient of the liquid on the different plates in the column. In this way nearly adiabatic conditions will prevail around the column and maximum efficiency in the distillation will be obtained.

If the distillation is carried out in an atmosphere of CO_2, the gas is passed in through the gas inlet (for details see fig. 2) at a rate of about 20 bubbles per minute.

If the still is to be cleaned after a distillation, the residue in the still pot is sucked out through the thermometer tube (No. 5 in fig. 1) after which the column is cleaned by one of the following methods:

1. Most of the liquid in the column is drawn into the still pot by applying suction at the thermometer tube (No. 5 in fig. 1). The

[11] Otto R. Greiner, 68 Marshall St., Newark, N. J.; E. Machlett and Sons, 50 William St., Long Island City, N. Y.

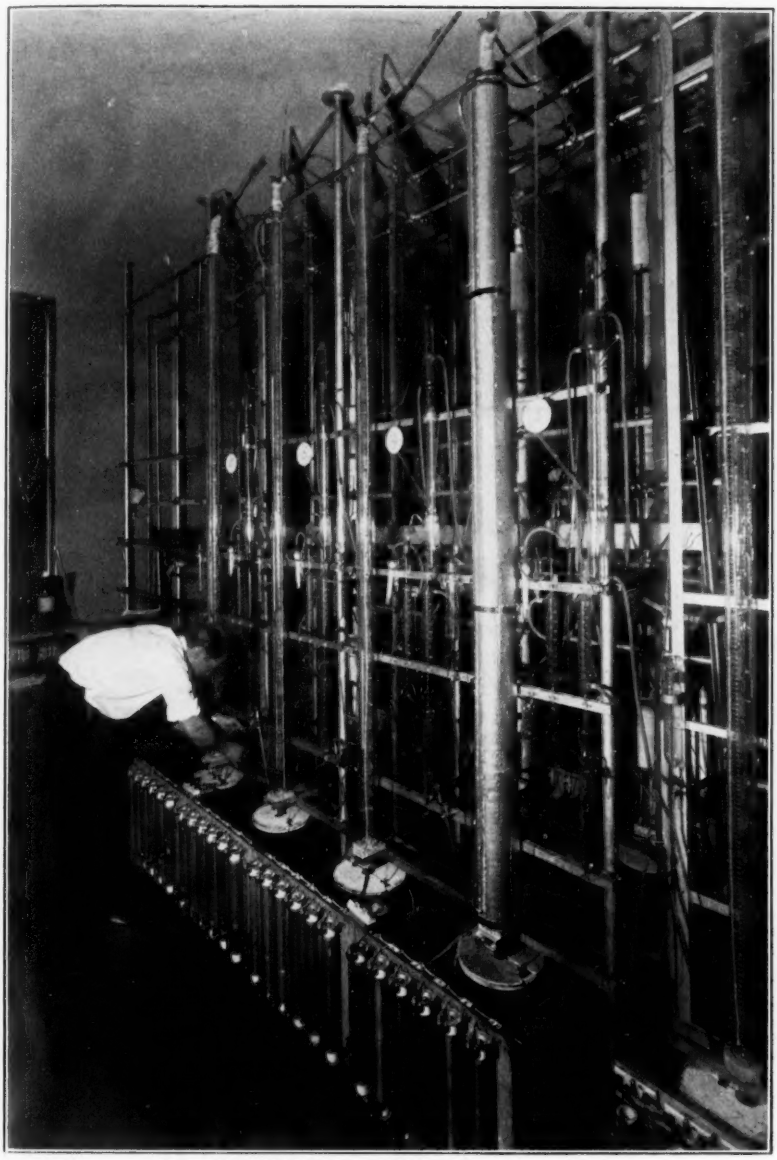


FIGURE 16.—*Assembly of five 30-plate bubbling cap stills mounted on a single frame*

remaining liquid is distilled into the receiver by heating the column jacket and drawing air (or an inert gas) through the column by applying suction at the top of condenser, *14*, Figure 1.

2. All of the liquid in the column is washed down into the still pot by means of a liquid poured into the thermometer tube at the top of the still. In the case of petroleum fractions, liquids such as water, methyl alcohol, or acetone may be used for this purpose, because they can afterwards be easily separated from the hydrocarbons. Water is, of course, separated by means of a separatory funnel, while acetone and methyl alcohol are removed from the hydrocarbons by repeated washing with water.[12] The wash liquid is then removed from the column by method (1). By the use of the above methods a 30-plate column can be cleaned out and dried in about 20 to 30 minutes.

XIII. COLUMNS FOR DISTILLATIONS AT PRESSURES LESS THAN 50 mm

For fractional distillations at low pressures, a packed column should be used. A laboratory still for vacuum distillation provided with a column packed with steel jack chain has been described elsewhere.[13] [14] If a high degree of separation is desired, a tall column should be employed. Figure 17 shows an all-glass rectifying still with an 11 m column packed with chromium-plated steel jack chain. When the height of a column reaches such a magnitude the combined weights of the packing, the column, and the column jacket will be considerable, and a special method of mounting becomes necessary. As shown in the figure a part (about 60 per cent) of this weight is carried by the counterweights, *W*, at the top of the still, so that no strains are introduced into the glass column or glass-column jacket when these expand or contract. The bottom support and other features of construction are similar to those of the bubble-cap stills already described.

Comparative runs with varying amounts of liquid in the column indicated that the efficiency of this still was greatest when there was flowing through the column a steady trickle of liquid, sufficient to wet the packing thoroughly. When operated just below the flooding point, the efficiency was materially decreased.

XIV. STOPCOCK LUBRICANT

The stopcocks throughout the distillation system should be lubricated, preferably with a lubricant which is insoluble or only slightly soluble in the liquids to be distilled. The selection of a suitable lubricant will therefore depend upon the physical and chemical nature of the distillate. Upon suggestion of T. P. Sager, of this bureau, polymerized diethylenephtalate and triethylenephtalate were tried as stopcock lubricant for distillation of petroleum fractions. While both of these compounds [15] are practically insoluble in most hydro-

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[12] See J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, p. 933; 1930.
[13] J. H. Bruun, B. S. Jour. Research, vol. 2, p. 476; 1929.
[14] This packing has been recommended by Dean, Hill, Smith, and Jacobs, Bur. of Mines Bull. 207, p. 9, 1922, and has been used in several stills at the Bureau of Standards.
[15] The preparation of these compounds has been described by W. H. Carothers and J. A. Arvin, J. Am. Chem. Soc., vol. 51, p. 2568, 1929, and by R. H. Kienle and A. G. Hovey, J. Chem. Soc., vol. 51, p. 509, 1929, and vol. 52, p. 3636, 1930.

carbons they can easily be removed from the stopcocks by washing with acetone in which they are soluble. In order to obtain a lubricant of suitable consistency, we melted about 20 per cent of the polymerized triethylenephtalate with about 80 per cent of the polymerized diethylenephtalate. This mixture has been found to be a very satisfactory stopcock lubricant for distillation of petroleum fractions and hydrocarbons.

The stopcock on the reflux regulator shown in Figure 9 has been lubricated with a special lubricant, which has a softening point of 50° to 60° C. This lubricant was suggested by C. H. Binkley, of this bureau, and was prepared by heating equal mols of sebasic acid and ethylene glycol for about 20 hours at 180° C. or about 15 hours at 200° C. The lubricant thus obtained is insoluble in aliphatic hydrocarbons, alcohol, and ether but is readily soluble in benzene, alkylhalides, and pyridine. For inorganic lubricants the reader is referred to recent papers by W. A. Boughton.[16]

XV. EFFICIENCY OF THE STILLS

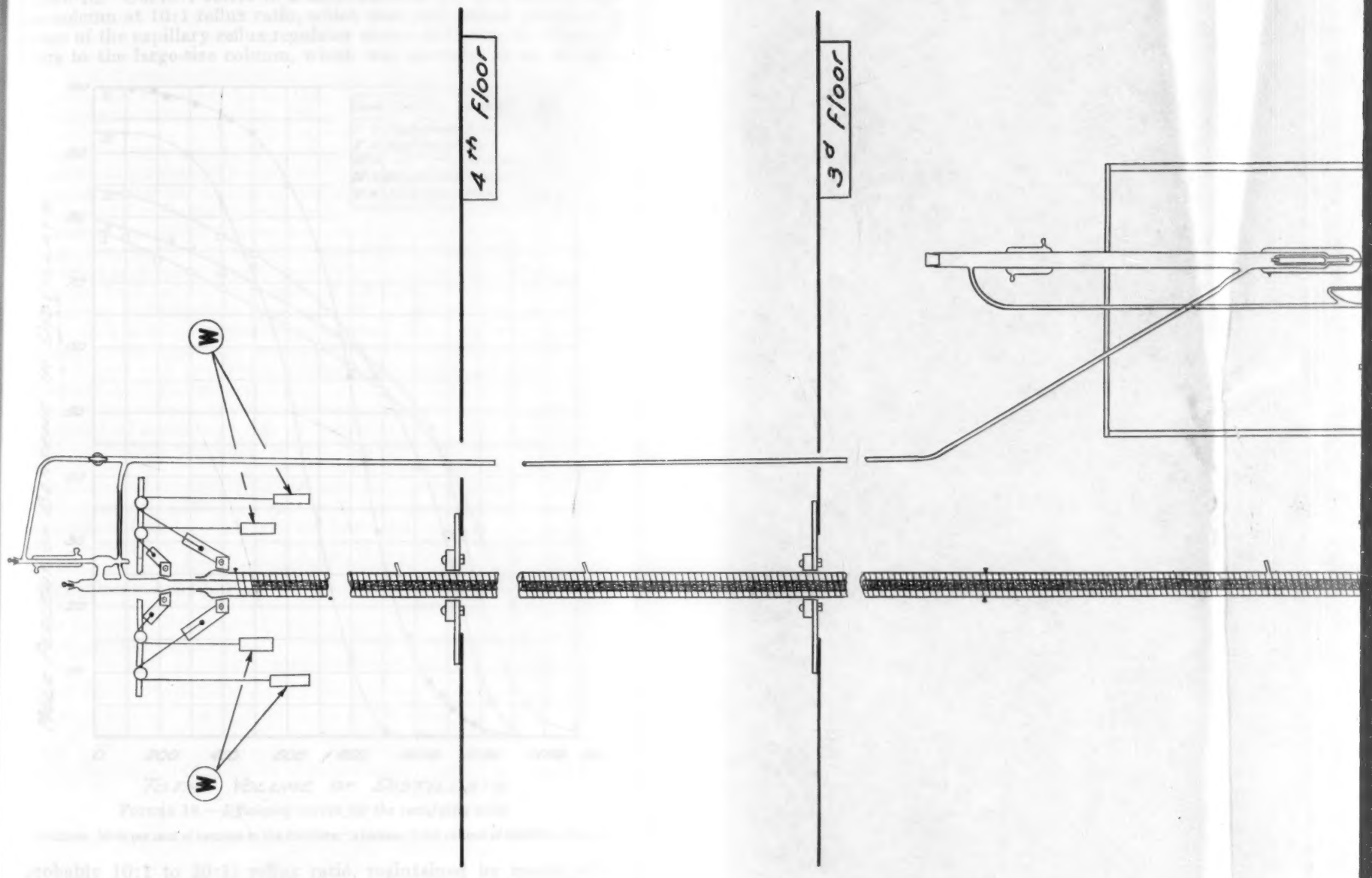
Many laboratory stills have been described in the literature in recent years. Distillations of various known mixtures have been carried out in these stills in order to illustrate their efficiencies. Unfortunately, however, a great many of these so-called efficiency tests give only the temperature-volume curve of the distillations as the criterion of efficiency. It is evident that an efficiency test based solely upon this curve is illusory and of little value, particularly if the components of the distilling mixture differ in boiling points by only a few degrees. The boiling range of a fraction may be a very unsatisfactory criterion for the composition of the distillates, because comparatively small differences in boiling points may correspond to large differences in composition. Moreover, the distillation temperatures, when measured in the usual manner, are influenced by many factors such as superheating of the vapor, rates of distillation, variations in the atmospheric pressure, etc.

During distillations at constant but very low rates, of mixtures consisting of substances which differ in boiling point by only a few degrees it is possible to obtain ordinary temperature readings at the still head which continuously indicate that the lower boiling constituent distills over at a concentration of about 100 per cent, while an accurate analysis might show that the distillate contains only 60 to 80 per cent of the lower boiling components. Extreme discrepancies like these are caused by the fact that the thermometer is not surrounded by vapor in sufficient quantities to register the true condensation temperature of the vapor mixture.

A more reliable method of determining the operating efficiency of a given still, which has been used by many investigators, is to analyze the distillates by some reliable method, and then to plot the composition-volume curve for a distillation under controlled conditions (i. e., with respect to reflux ratio, rate of distillation, etc.). The operating efficiencies of the rectifying columns described in this paper were determined by this method, using the following binary mixture.[17]

Benzene (boiling point 80.2° C.)	50 mole per cent.
Ethylene chloride (boiling point 83.7° C.)	50 mole per cent.

[16] W. A. Boughton, J. Am. Chem. Soc., vol. 52, pp. 2421, 2813, 4335, 4858; 1930.
[17] Suggested by E. W. Washburn. For details see Appendix II.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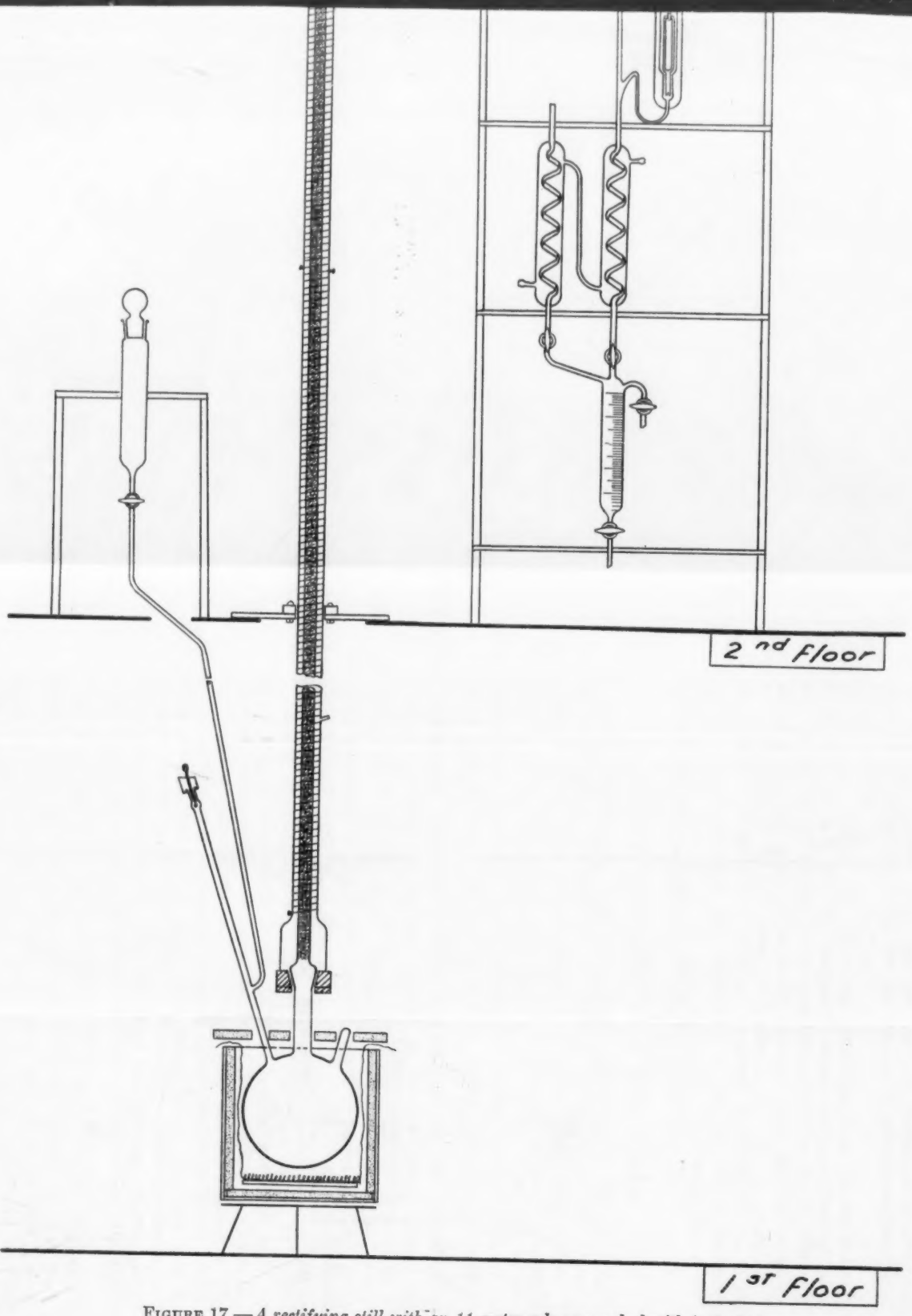

FIGURE 17.—*A rectifying still with an 11-meter column packed with jack chain*

70688—31. (Face p. 872.)

The initial charge as well as the distillates were analyzed by determining their refractive indices, after which the composition-volume curves for the distillations were plotted. These curves are shown in Figure 18. Curve *I* refers to a distillation in the 30-plate medium-size column at 10:1 reflux ratio, which was maintained constant by means of the capillary reflux regulator shown in Figure 10. Curve *II* refers to the large-size column, which was operated at an unknown

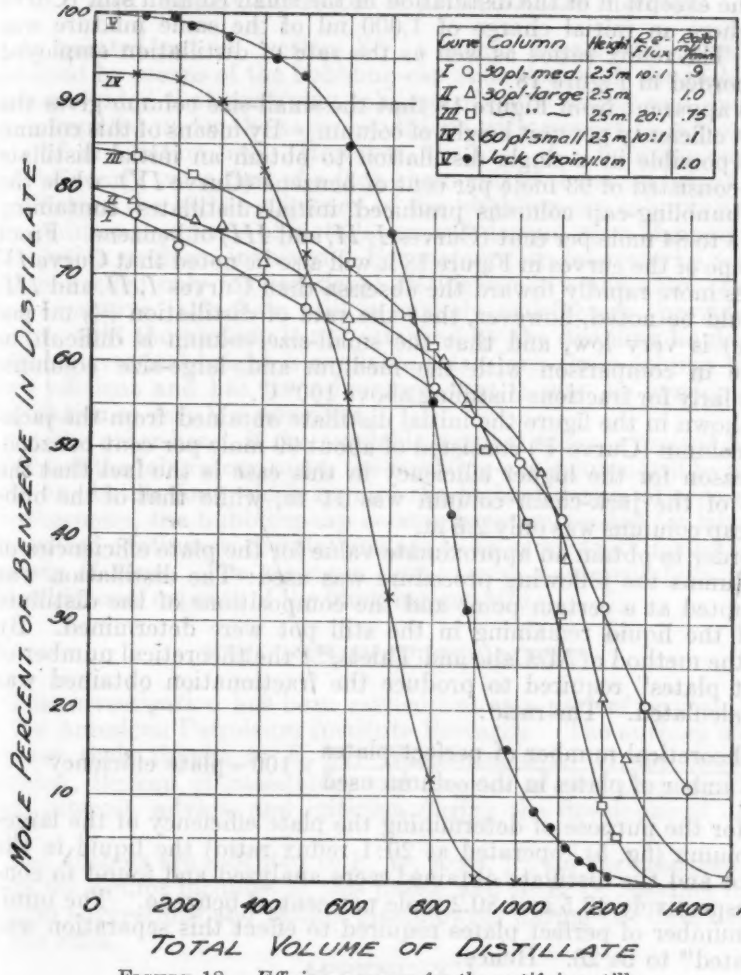

FIGURE 18.—*Efficiency curves for the rectifying stills*

Ordinate: Mole per cent of benzene in the distillate. Abscicca: Total volume of distillate collected.

(probably 10:1 to 20:1) reflux ratio, maintained by means of the reflux regulator shown in Figure 9. Curve *III* shows the results of a distillation in the same 30-plate large-size column, but the distillation was in this case carried out at a reflux ratio of 20:1. Curve *IV* is the composition-volume curve for a distillation in the 60-plate small size still which was operated at a reflux ratio of 10:1. The heights of all these columns were about 2.5 m.

For comparison, a distillation was carried out in the jack-chain packed-column still (shown in fig. 17), the column of which was 11 m high (or 4.5 times as high as the bubbling-cap stills.) This distillation, which was carried out at a reflux ratio of about 15:1, gave Curve *V*, Figure 18. This is also reproduced in Figures 23 and 24.

The initial charge for these distillations was in every case 1,500 ml of a 50:50 mole per cent mixture of benzene and ethylene chloride, with the exception of the distillation in the small column still (Curve IV), where an initial charge of 1,000 ml of the same mixture was used. The reflux ratios as well as the rate of distillation employed are recorded in Figure 18.

It is apparent from Figure 18 that the small-size column gives the highest efficiency per unit height of column. By means of this column it was possible in a single distillation to obtain an initial distillate which consisted of 93 mole per cent of benzene (Curve *IV*), while the other bubbling-cap columns produced initial distillates containing from 78 to 84 mole per cent (Curves *I*, *II*, and *III*) of benzene. From the shape of the curves in Figure 18 it will also be noted that Curve *IV* declines more rapidly toward the abscissa than Curves *I*, *II*, and *III*. It should be noted, however, that the rate of distillation (⅒ ml per minute) is very low, and that the small-size column is difficult to operate in comparison with the medium and large-size columns, particularly for fractions distilling above 100° C.

As shown in the figure the initial distillate obtained from the jack-chain column (Curve *V*) consisted of about 99 mole per cent benzene. The reason for the higher efficiency in this case is the fact that the height of the jack-chain column was 11 m, while that of the bubbling-cap columns was only 2.5 m.

In order to obtain an approximate value for the plate efficiencies of the columns the following procedure was used: The distillation was interrupted at a certain point and the compositions of the distillate and of the liquid remaining in the still pot were determined. By using the method of McCabe and Thiele,[18] "the theoretical number of perfect plates" required to produce the fractionation obtained was then calculated. The ratio:

$$\frac{\text{Theoretical number of perfect plates}}{\text{Number of plates in the column used}} \times 100 = \text{plate efficiency}$$

Thus for the purpose of determining the plate efficiency of the large-size column (fig. 5) (operated at 20:1 reflux ratio) the liquid in the still pot and the distillate obtained were analyzed and found to contain respectively 43.5 and 80.2 mole per cent of benzene. The minimum number of perfect plates required to effect this separation was calculated[18] to be 26. Hence:

$$\frac{26}{30} \times 100 = 87 \text{ per cent plate efficiency}$$

which represents a very satisfactory efficiency for a laboratory column.

Because of the difficulties involved in maintaining perfectly adiabatic conditions around a rectifying column of small diameter, it is probable that even if a constant reflux ratio (20:1) at the top of the

[18] W. L. McCabe and E. W. Thiele, Ind. Eng. Chem., vol. 17, p. 605; 1925.

column is maintained, the reflux may be somewhat increased in the lower parts of the column. This increase is due to the condensation which results from the loss of heat from the column to the surrounding column jacket. In view of this slight uncertainty in the reflux ratio the calculated plate efficiency should be considered only as an approximate value.

XVI. SELECTION OF A LABORATORY STILL

As pointed out in Section XV, a higher degree of separation is obtained by means of the bubbling-cap stills than with the jack-chain stills provided that rectifying columns of equal height and diameter are compared under the same conditions with respect to reflux ratio, rate of distillation, etc. However, the cost of a bubbling-cap still will be nearly twice that of a jack-chain still of the same height.

Whether the higher efficiency of the bubbling-cap column justifies the additional expense of installation will depend upon the particular distillation problem involved. For instance, in laboratories where a still is needed only for occasional distillation it would seem that the less expensive jack-chain still is entirely satisfactory, provided, of course, that the packing is not attacked by the distilling liquids. If sufficient vertical height is available a tall jack-chain column will be very efficient and has the advantage that it may be employed for distillation at very low pressures.

On the other hand, if the available vertical space is limited by the height of the laboratory room, the bubbling-cap column will be preferable for distillations which require the highest degree of separation. Furthermore, the bubbling-cap column is recommended for laboratories where continuous distillations are to be carried out during longer periods of time. The saving in time in such a case will fully justify the additional expense of the bubbling-cap still.

XVII. ACKNOWLEDGMENT

This investigation has been carried out as a part of project No. 6 of the American Petroleum Institute Research. The authors wish to express their thanks to E. W. Washburn, chief of the chemistry division, Bureau of Standards, and director of this project, for his kind interest, advice, and criticism during the development of this work.

The authors are indebted to F. W. Rose, jr., for his preparation of all of the figures included in this paper, and to E. O. Sperling for his helpful suggestions and skillful glassblowing during the development of the stills.

APPENDIX 1

REGULATION OF THE PRESSURE WITHIN THE STILL ASSEMBLY

In order to maintain a constant pressure during the distillations, the arrangement shown in Figure 19 is used. The rectifying stills indicated by the small circles, *S*, are connected directly to the main pressure line and to a welded 350-liter steel tank, *B*, which prevents

sudden changes in pressure. The main pressure line is connected through a cooling trap, *T*, to a vacuum pump, *P*, the manostat, *N*, and the manometer, *M*.

The manostat is connected to the relay, *R*, which starts the pump, *P*, when the pressure increases about 0.05 mm in the still assembly. An inclined butyl phthalate manometer (not shown in the figure) is used as a pressure gage. This is designed so as to restrict the total pressure change to the sloping end of the manometer. A movement of 0.6 mm of the meniscus corresponds to a pressure change of 0.01 mm mercury within the system.

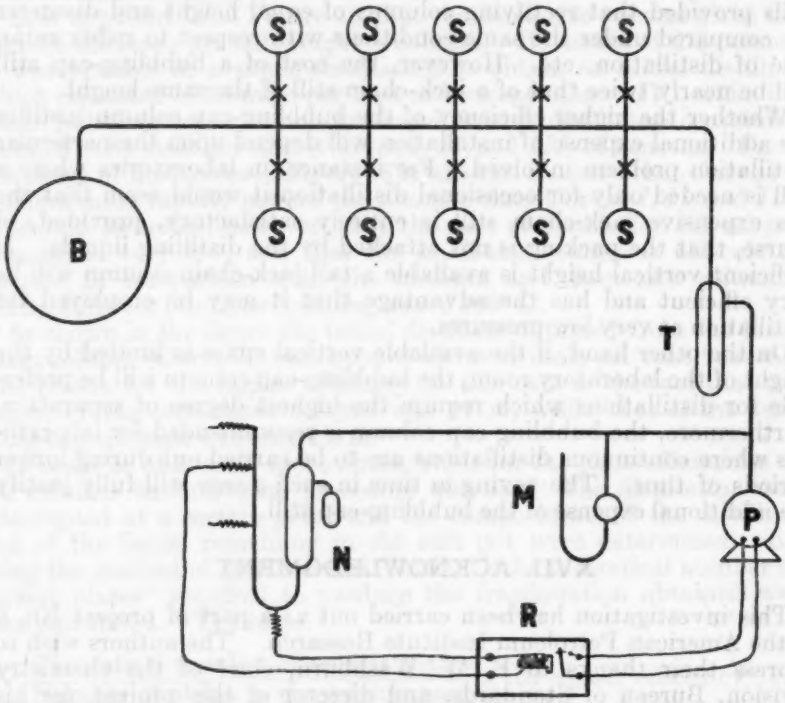

FIGURE 19.—*Diagram showing the method used for regulation of the pressure within the still assembly*

Figure 20 is a working drawing of the manostat.[19] The tungsten lead, 1, is permanently connected to one terminal of the relay. (See fig. 19.) The other relay terminal is connected to the tungsten lead, 2, 3, or 4, depending upon the desired pressure. The working pressure range for the manostat in Figure 20 is from 25 to 215 mm. The three contact points, 2, 3, and 4, are for pressures of 100, 150, and 215 mm, respectively. Intermediate pressures can be obtained by increasing or decreasing the level of mercury in bulb, *U*, by tilting the apparatus to adjust the amount of mercury in the auxiliary bulb, *V*. More refined adjustment is obtained by having the manostat so mounted that by tilting it sideways the mercury levels can be changed

[19] This is a modification of a pressure regulator described by H. L. Cox, Ind. Eng. Chem., Anal. Ed., vol. 1, p. 7; 1929.

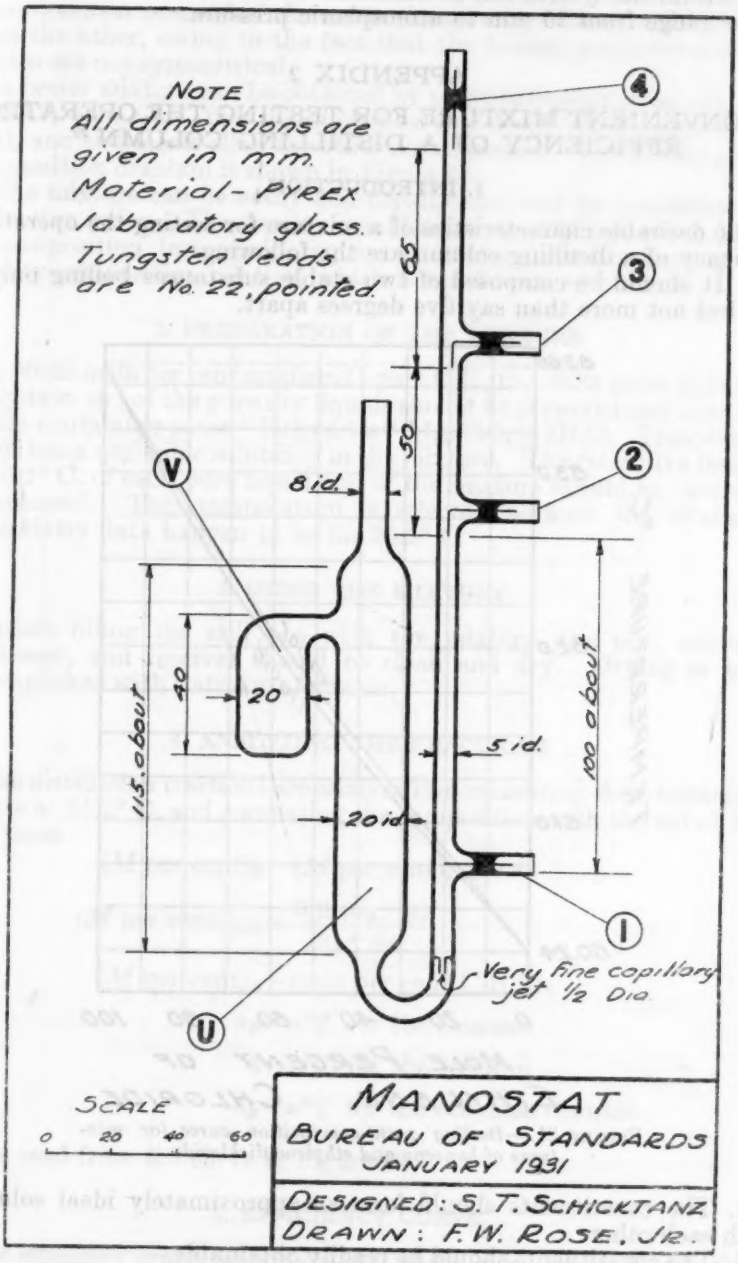

FIGURE 20.—*The manostat*

by a small fraction of a millimeter. With this arrangement the pressure within the system can be maintained constant to about 0.05 mm in the range from 25 mm to atmospheric pressure.

APPENDIX 2

A CONVENIENT MIXTURE FOR TESTING THE OPERATING EFFICIENCY OF A DISTILLING COLUMN [20]

1. INTRODUCTION

The desirable characteristics of a mixture for testing the operating efficiency of a distilling column are the following:

1. It should be composed of two stable substances boiling only a few but not more than say five degrees apart.

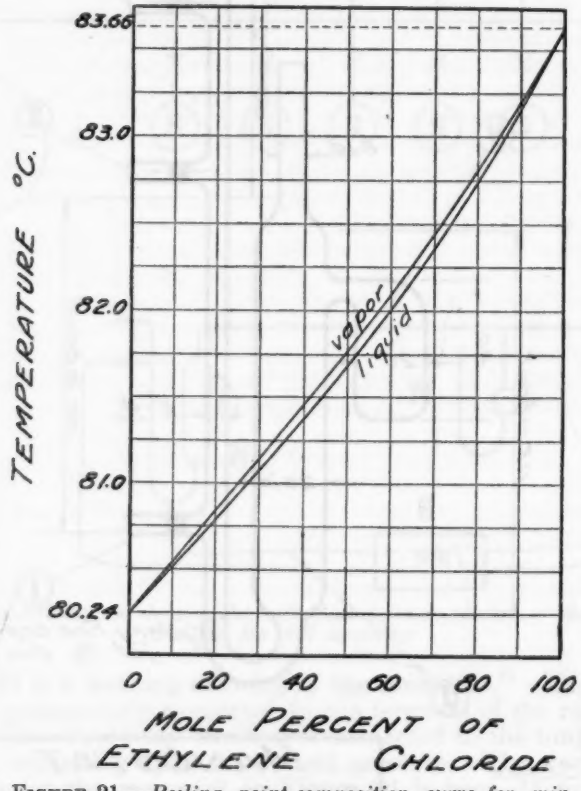

FIGURE 21.—*Boiling point-composition curve for mixtures of benzene and ethylene dichloride*

2. The constituents should form an approximately ideal solution with each other.

3. The constituents should be readily obtainable.

4. A convenient method for the rapid and accurate analysis of the mixture should be available.

[20] Issued originally as Bureau o Standards Letter Circular No. 269; October, 1930.

A mixture of CCl_4 and C_6H_6 meets all of the above requirements except No. 2. Failure to meet this requirement means that fractionation near one end of the composition range is more difficult than near the other, owing to the fact that the boiling point-composition curves are not symmetrical.

A better mixture can be obtained by substituting ethylene chloride, $C_2H_4Cl_2$, for CCl_4. This liquid forms a practically ideal solution with C_6H_6 and also meets all of the other requirements. The boiling point-composition diagram is shown in Figure 21.

The mixture can be easily and rapidly analyzed by measuring the refractive index. The density would serve equally well as an index of composition but would require a careful determination of the density-composition relation, which is not known at present.

2. PREPARATION OF THE MIXTURE

A 50-50 mole per cent mixture (1 part C_6H_6 to 1.2683 parts $C_2H_4Cl_2$, weights in air) of the pure dry liquids should be prepared and kept in a bottle containing some "Dehydrite" $Mg(ClO_4)_2 \cdot 3H_2O$. This drying agent has a negligible solubility in the mixture. The refractive indices at 25.2° C. of each pure liquid and of the mixture should be carefully determined. This temperature is selected because the available refractivity data happen to be for 25.2° C.

3. USING THE MIXTURE

Before filling the still pot with the mixture, the pot, column, condenser, and receiver should be clean and dry. Drying is best accomplished with a stream of dry air.

4. ANALYZING THE FRACTIONS

The distillation fractions are analyzed by measuring their refractive indices at 25.2° C. and computing the composition with the aid of the equations

$$(M \text{ per cent})_E = (M \text{ per cent})_{\text{calc.}} - \Delta$$

$$(M \text{ per cent})_{\text{calc.}} = \frac{100\ (n_B - n)}{n_B - n_E}$$

$(M \text{ per cent})_E$ = mole per cent $C_2H_4Cl_2$

$n_B = n_D^{25.2°}$ for the benzene

$n = n_D^{25.2°}$ for the fraction

$n_E = n_D^{25.2°}$ for the ethylene chloride

Δ is read from the curve in Figure 22.

5. EFFICIENCY CURVE

The efficiency graph for a given still and a given mode of operation is obtained by plotting volume of fraction against composition as illustrated in Figure 23 or by making the corresponding differential plot as illustrated in Figure 24.

After completing the test the fractions may be returned to the stock bottle, the contents of which can be kept at the 50–50 composition by "doctoring" occasionally with a little of the required pure component until the original refractive index is restored.

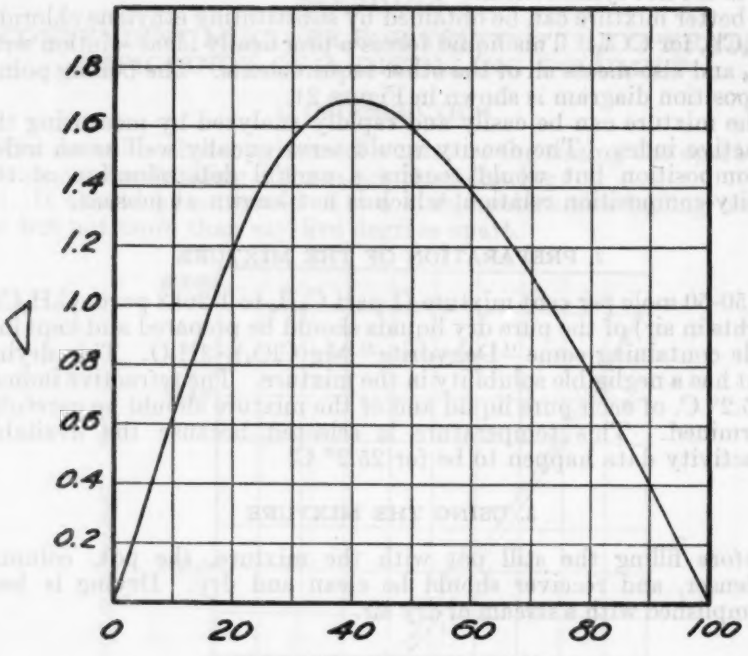

FIGURE 22.—*Correction curve for the refractive index*

6. PURIFICATION OF THE CONSTITUENTS

(a) ETHYLENE CHLORIDE

Ethylene chloride, equal in quality to the best grade made by Eastman, required to be distilled only once from a suitable drying agent (Dehydrite) in a good column still with rejection of the initial and final fractions.

Yield, about 85 volume per cent.

$n_D^{25.2°}$ is 1.4418.

Freezing range: 34.9° to 35.1° C.

(b) BENZENE

A good grade of C. P. benzene should be selected and treated as follows:

(1) Wash for 1 hour (preferably in a shaking machine) with 0.1 of its volume of C. P. concentrated H_2SO_4.

(2) Wash successively with water, dilute NaOH and water.

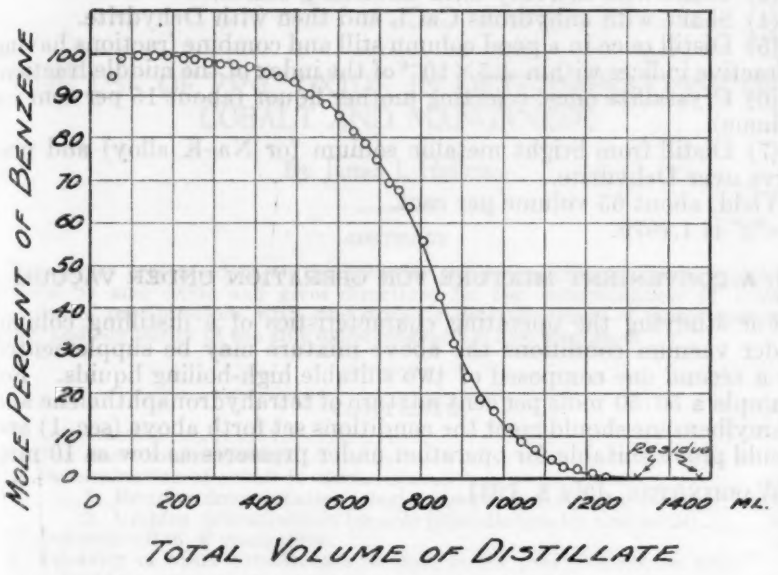

FIGURE 23.—*Efficiency test of an 11-meter packed column*

Ordinate: Mol per cent of benzene in distillate. Abscissa: Total volume of distillate collected.

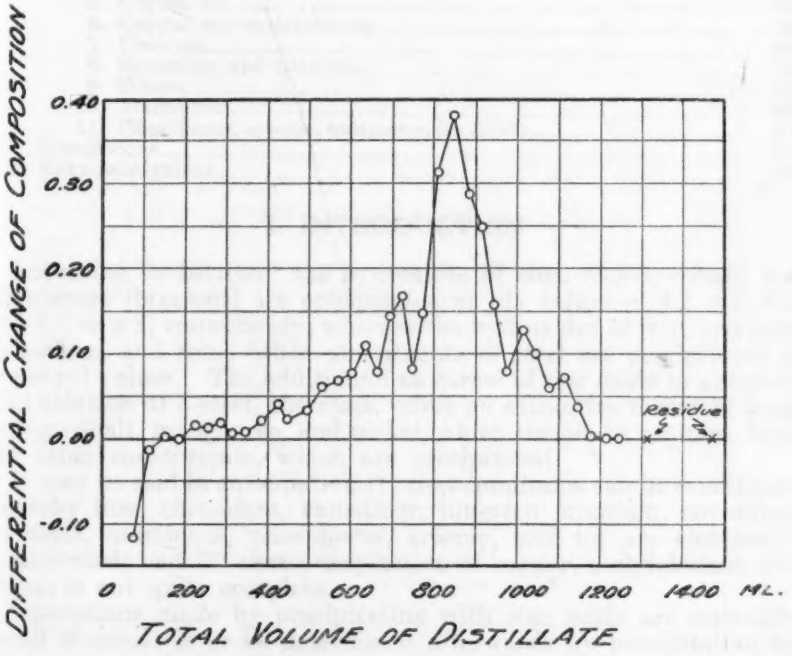

FIGURE 24.—*Differential graph of Figure 23*

(3) Shake with mercury until tarnishing ceases.
(4) Shake with anhydrous $CaCl_2$ and then with Dehydrite.
(5) Distill once in a good column still and combine fractions having refractive indices within $\pm 5 \times 10^{-4}$ of the index of the middle fraction.
(6) Crystallize once, rejecting mother liquor (about 15 per cent by volume).
(7) Distill from bright metallic sodium (or Na–K alloy) and preserve over Dehydrite.

Yield, about 65 volume per cent.
$n_D^{25.2°}$ is 1.4976.

7. A CONVENIENT MIXTURE FOR OPERATION UNDER VACUUM

For studying the operating characteristics of a distilling column under vacuum conditions the above mixture may be supplemented by a second one composed of two suitable high-boiling liquids. For example a 50:50 mole per cent mixture of tetrahydronaphthalene and *n*-amylbenzene should meet the conditions set forth above (sec. 1) and should prove suitable for operation under pressures as low as 10 mm.

WASHINGTON, July 8, 1931.

THE USE OF ZINC OXIDE IN DETERMINATIONS OF COBALT AND MANGANESE

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ABSTRACT

This paper presents data on the behavior of the constituents of steel in precipitations by zinc oxide and gives directions for the determination of cobalt. The use of precipitations with zinc oxide in determinations of manganese and nickel and the purity of the zinc oxide reagent are also discussed.

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I. INTRODUCTION

According to Britton [1] the hydroxides of zinc, nickel, cobalt, and manganese (bivalent) are precipitated at pH values of 5.2, 6.7, 6.8, and 8.5 to 8.8, respectively, whereas the hydroxides of iron, trivalent chromium, and some other constituents of steel are precipitated at lower pH values. The addition of an excess of zinc oxide to a slightly acid solution of a steel, therefore, offers an attractive means of separating cobalt, manganese, and nickel, which remain in solution, from the other constituents, which are precipitated.

It may be said in anticipation (1) that conditions can be established whereby iron, chromium, vanadium, tungsten, uranium, zirconium, titanium, aluminum, phosphorus, arsenic, and tin are completely precipitated; and (2) that precipitation of copper, molybdenum, and silicon is not quite complete.

Separations made by precipitating with zinc oxide are especially useful if cobalt is to be determined afterwards by precipitation by

[1] H. T. S. Britton, Hydrogen Ions, p. 278, 1929 ed., D. Van Nostrand Co.

α-nitroso-β-naphthol, and find occasional application in determinations of manganese in steel containing much chromium or vanadium. Most textbooks recommend precipitation by zinc oxide for the separation of manganese or cobalt from the other constituents of steel if subsequent operations require the absence of these constituents. Some recommend that the precipitation be made in hot solutions; others prescribe cold solutions.[2] None of these gives any data with respect to the completeness of the separation. As works and commercial laboratories at present are using the method for the determination of cobalt and manganese, it seems desirable that such data should be presented. There are many variations of minor details of the method, but the procedure described in Section III for the determination of cobalt in high-speed steels by making a single precipitation is typical of these procedures. In all instances in which precipitations by zinc oxide were made in hot solutions (see Tables 1, 2, and 3) the solutions were cooled to room temperature before filtering.

II. THE ZINC OXIDE REAGENT

The suspension of zinc oxide used in this work was prepared by thoroughly shaking 50 g of the finely powdered reagent with 300 ml of water. Ten ml of this suspension remained colorless upon addition of two drops of a 1 per cent solution of phenolphthalein, thus showing the absence of sodium carbonate. Lord and Demorest[3] state that the zinc oxide should not contain any alkali, because this would precipitate manganese (also nickel and cobalt). Owing to the slight excess of reagent added, a small contamination by sodium carbonate does not affect the results seriously, as is shown by the following tests.

Precipitates obtained by double precipitations with zinc oxide as described in the determination of cobalt (Section III) were dissolved and analyzed for cobalt, manganese, and nickel. The tests were made on three steels containing 5 per cent of cobalt, 0.94 per cent of manganese, and 8.44 per cent of nickel, respectively. Three different reagents were used, and the suspensions were prepared as described. The first was the ordinary reagent, which showed no alkaline reaction with phenolphthalein; the second was the same reagent, to which 0.1 per cent of sodium carbonate was added and intimately ground in a mortar; the third was a similarly prepared reagent containing 0.5 per cent of sodium carbonate. The precipitates obtained by the use of the ordinary reagent showed 0.01 per cent of cobalt, no manganese, and 0.09 per cent of nickel; those with the reagent containing 0.1 per cent of sodium carbonate showed 0.02 per cent of cobalt, no manganese, and 0.10 per cent of nickel; and those with the reagent containing 0.5 per cent of sodium carbonate showed 0.02 per cent of cobalt, no manganese, and 0.10 per cent of nickel. It is obvious, however, that a large excess of a reagent containing sodium carbonate would precipitate cobalt, manganese, and nickel, and that a reagent that does not give an alkaline reaction with phenolphthalein should be used.

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[2] N. W. Lord and D. J. Demorest, Metallurgical Analysis, p. 82, 1924 ed., McGraw-Hill Book Co., recommend precipitation in a hot solution. F. T. Sisco, Analysis of Steel, p. 229, 1923 ed., McGraw-Hill Book Co., recommends precipitation in a cold solution. W. A. Naish and J. E. Clennell, Select Methods of Metallurgical Aanalysis, p. 365, 1930 ed., J. Wiley & Sons, recommend that an excess of ZnO be added and the solution then boiled for 10 minutes in the determination of cobalt in steel.

[3] N. W. Lord and D. J. Demorest, Metallurgical Analysis, p. 82, 1924 ed., McGraw-Hill Book Co.

III. DETERMINATION OF COBALT IN STEEL

The following procedures were used in the determination of cobalt in the experimental work, and are recommended for the determination of cobalt in steels. In these methods iron and most of the elements that interfere are separated from cobalt by single or double precipitations with zinc oxide followed by filtration. The cobalt is then precipitated in the filtrate by α-nitroso-β-naphthol and ignited to the oxide or the metal. Besides iron, the elements that interfere in a precipitation by α-nitroso-β-naphthol and which may be present in steel are copper, chromium, vanadium, tungsten, molybdenum, tin, and antimony.

1. ROUTINE DETERMINATION OF COBALT IN STEEL (SINGLE PRECIPITATION BY ZINC OXIDE)

Transfer 2.00 g of sample to a 600 ml beaker, add 50 ml of dilute hydrochloric acid (1:1), heat, and when decomposition is complete, add 10 ml of dilute nitric acid (1:1) to oxidize the iron and tungsten. Evaporate until salts begin to separate (5 to 10 ml), and then add 100 ml of hot water. Digest on the steam bath for a few minutes, and transfer the contents of the beaker to a 500 ml volumetric flask. Dilute to about 300 ml, and add a freshly prepared suspension of zinc oxide in portions of about 5 ml until the iron is precipitated and a slight excess of zinc oxide is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient zinc oxide has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess of zinc oxide is also indicated by a slightly white and milky supernatant liquid.

Dilute to the mark, mix thoroughly, and transfer the contents of the flask to the original dry beaker. Allow the precipitate to settle, and filter through a dry paper. Discard the first 10 to 15 ml of filtrate, and then catch exactly 250 ml in a dry volumetric flask. Transfer the solution to a 600 ml beaker, add 10 ml of hydrochloric acid, and dilute to about 400 ml.

Heat the solution to boiling, and add 6 ml of α-nitroso-β-naphthol solution [4] for every 0.01 g of cobalt present. Allow the solution to cool for one-half to two hours, and filter through a No. 40 Whatman or similar paper. The filtration proceeds best if the precipitate is thoroughly stirred as the solution is poured on the paper. Transfer all of the precipitate to the filter and wash thoroughly with hot dilute hydrochloric acid (1:2) and then with hot water.

Transfer the paper and precipitate to a weighed porcelain crucible, and ignite slowly at first (preferably in a muffle) and finally at 750°–900° C. Heating above 900° C. has a tendency to convert Co_3O_4 to CoO.[5] Cool, and weigh as Co_3O_4, which contains 73.4 per cent of cobalt.

A blank should be taken through all steps of the determination. A 2 g sample of Bureau of Standards ingot iron No. 55 or chrome-tungsten-vanadium steel No. 50a is satisfactory for this purpose.

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[4] Prepare by dissolving 1 g of the dry reagent in 15 ml of glacial acetic acid and filtering.

[5] Ignition at 1,000° C., or higher, converts Co_3O_4 almost quantitatively to CoO, and application of the factor for cobalt in Co_3O_4(0.734) to the oxide, CoO, would yield a result of 4.67 in a steel that contains 5.00 per cent of cobalt. This error can be avoided by reducing the oxide in hydrogen and weighing the metal

Any similar material known to be free from cobalt should also be satisfactory. It is especially important that the same quantity of α-nitroso-β-naphthol be used in the blank run as in the determination. A litte macerated paper added to the blank after the α-nitroso-β-naphthol reagent facilitates filtration and washing.

TABLE 1.—*Results for cobalt obtained by precipitation by α-nitroso-β-naphthol after a single precipitation by zinc oxide*

No.	Material analyzed	Cobalt[1] added	Cobalt found weighed as—		Error (based on difference between amount added and amount found by ignition in H_2)	Other elements added	Temperature of ZnO precipitation
			Co metal after reduction in H_2	Co_3O_4 ignited at 750°–850° C.			
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
1	2 g B. S. ingot iron No. 55	3.65	3.56	3.57	−0.09	None	20° to 30° C.
2	do	3.65	3.52	3.50	−.13	do	Do.
3	2 g B. S. Cr-W-V steel No. 50a[2].	3.65	3.50	3.48	−.15	do	Do.
4	do	3.65	3.50	3.48	−.15	do	Do.
5	do	4.83	4.60	4.57	−.23	do	Do.
6	do	4.83	4.60	4.59	−.23	do	Do.
7	do	2.42	2.35	2.35	−.07	do	Do.
8	1 g B. S. Cr-W-V steel No. 50a.	2.42	[3] 2.36	2.34	−.06	do	Do.
9	2 g B. S. Cr-W-V steel No. 50a.	4.83	4.59	4.56	−.24	do	100° C.—cooled before filtering.
10	do	4.83	[4] 4.52	4.51	−.31	0.5 Cu+0.5 Mo	
11	do	4.83	[5] 4.60	.....	−.23	do	20° to 30° C.
12	do	4.83	[5] 4.70	.....	−.13	0.5 Mo	Do.
13	do	4.83	[5] 4.64	.....	−.19	0.5 Cu	Do.
14	1 g B. S. Cr-W-V steel No. 50a.	9.66	9.35	9.32	−.31	None	Do.
15	do	9.66	9.34	9.32	−.32	do	Do.

[1] The cobalt was added (before the sample was dissolved) in the form of a solution of cobalt sulphate which was standardized (1) by deposition of the metal by electrolysis, making proper corrections for nickel and sulphur; and (2) by precipitation with α-nitroso-β-naphthol, ignition to oxide, and weighing as metal after reducing the oxide in hydrogen.

[2] This steel has the following percentage composition: C, 0.66; Mn, 0.287; P, 0.020; S, 0.007; Si, 0.48; W, 18.25; Cr, 3.52; V, 0.97; Cu, 0.047; Ni, 0.045; Co, none found.

[3] After removing the aliquot portion of the filtrate obtained in the precipitation by zinc oxide as described in the method, the filtration was continued, the precipitate was washed with water, and the filtrate and washings were reserved. The precipitate containing the iron, chromium, etc., was dissolved in HCl, and a second precipitation was made as described in the method that follows (Section III, 2). The filtrate and washings obtained in the second precipitation were combined with the reserved solution, and the cobalt was then determined. The total amount of cobalt found was exactly that originally added. This indicates that the low result obtained in the first portion was caused by retention of cobalt in the first precipitate.

[4] The ignited residue in this determination contained 1.1 mg of $CuO+MoO_3$. If no correction for this had been made, the result would have been 4.61 per cent.

[5] The ignited residue in these determinations contained from 0.8 to 1.2 mg of oxides of copper or molybdenum and the results would have been from 0.06 to 0.10 per cent higher if correction for these had not been made.

The data in Table 1 show that if only one precipitation by zinc oxide is made, results for cobalt in the percentages usually present in high-speed steels are likely to be from 0.1 to 0.3 per cent low as a result of retention of cobalt in the bulky precipitate. The temperature at which the precipitation is made has little or no effect on the results. If the temperature of ignition of the cobalt oxide exceeds 900° C., it is not unusual for results by this method to be as much as 0.5 per cent low in the case of steels containing approximately 5 per

cent of cobalt. The procedure (Section III, 2), involving two precipitations by zinc oxide, gives results which are more nearly correct, and it does not require much more of the analyst's time.

2. UMPIRE DETERMINATION OF COBALT IN STEEL (DOUBLE PRECIPITATION BY ZINC OXIDE)

Transfer 1.00 g of sample to a 400 ml beaker, add 25 ml of dilute hydrochloric acid (1:1), heat, and when decomposition is complete, add 5 ml of dilute nitric acid (1:1), to oxidize the iron and tungsten. Evaporate until salts begin to separate (about 5 ml). Add 100 ml of hot water, and digest on the steam bath for about five minutes. Dilute the solution to about 200 ml, and precipitate with zinc oxide as in 1.

Allow the precipitate to settle for a few minutes, and filter the solution through a 12.5 cm filter paper.[6] Wash the beaker and the precipitate on the filter three times with cold water. Reserve the filtrate and washings. When the filter has drained, transfer the paper and precipitate to the beaker in which the precipitation was made, add 12 ml of hydrochloric acid, and stir the paper to a pulp. The iron should now be in solution; if it is not, add more hydrochloric acid, avoiding a large excess. Dilute the solution to 200 ml, and repeat the precipitation with zinc oxide. Filter on a 15 cm paper, and wash four or five times with cold water.

Combine the two filtrates and washings, add 10 ml of hydrochloric acid, and adjust the volume to about 400 ml. Heat the solution to boiling, add 6 ml of α-nitroso-β-naphthol solution for every 0.01 g of cobalt present, and proceed as directed in the method previously described, paying particular attention to blank runs and to the temperature of ignition. Weighing as metal after reducing the oxide in hydrogen is to be preferred, especially if a muffle furnace with good temperature control is not available. If more than 0.2 per cent of copper or molybdenum is present, these should be determined in the ignited residue and the proper correction made. The results obtained by this method are shown in Table 2.

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[6] S & S No. 589 blue or white band and Whatman No. 40 or 42 papers are satisfactory. If the looser papers are used, a little finely divided ZnO may pass through the paper at first. This is unobjectionable, because zinc is not precipitated by α-nitroso-β-naphthol.

TABLE 2.—*Results for cobalt obtained by precipitation by α-nitroso-β-naphthol after a double precipitation by zinc oxide*

No.	Material analyzed	Cobalt[1] added	Cobalt found weighed as		Error (based on difference between amount added and amount found by ignition in H_2)	Other elements added	Temperature of ZnO precipitation
			Co metal after reduction in H_2	Co_3O_4 ignited at 750°–900° C.			
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
1	1 g B. S. ingot iron No. 55	3.65	3.63	3.58	−0.02	None	20° to 30° C.
2	do	3.65	3.65	3.65	.00	do	Do.
3	1 g B. S. Cr-W-V steel No. 50a[2]	3.65	3.63	3.60	−.02	do	Do.
4	do	3.65	3.67	3.64	+.02	do	Do.
5	do	.73	.71	.72	−.02	do	Do.
6	do	4.83	4.82	4.84	−.01	do	Do.
7	do	4.83	4.80	4.80	−.03	do	Do.
8	do	4.83	4.81		−.02	do	Do.
9	do	4.83	4.84	4.83	+.01	do	Do.
10	do	4.83	4.84		+.01	do	60° C.
11	do	4.83	4.84		+.01	do	100° C.
12	do	4.83	[3] 4.79		−.04	0.5 Cu	20° to 30° C.
13	do	4.83	[4] 4.80		−.03	0.5 Mo	Do.
14	do	4.83	[5] 4.79		−.04	0.5 Cu+0.5 Mo	Do.
15	do	4.83	[5] 4.77		−.06	do	Do.
[7]16	do	4.83	4.80		−.03	do	Do.
[7]17	do	4.83	4.85		+.02	do	Do.
[7]18	do	4.83	4.80	4.79	−.03	do	Do.
19	0.5 g B. S. Cr-W-V steel No. 50a	9.66	[6] 9.70	9.68	+.04	6.0 Ni	Do.
20	do	9.66	[6] 9.72	9.73	+.06	do	Do.
21	0.1 g B. S. Cr-W-V steel No. 50a[8]	.97	.98	.98	+.01	70 Cr+20 Ni	Do.
22	do	.19	.20	.20	+.01	do	Do.

[1] See footnote 1 under Table 1.
[2] See footnote 2 under Table 1.
[3] Metal contained 0.2 mg of copper. Uncorrected result was 4.81 per cent.
[4] Metal contained 0.9 mg of molybdenum. Uncorrected result was 4.89 per cent.
[5] Results corrected for copper and molybdenum.
[6] These results are uncorrected for nickel. They contained 0.02 per cent each.
[7] After the samples were decomposed and the tungsten oxidized, the copper and molybdenum were precipitated by hydrogen sulphide without first removing the tungstic acid. The tungstic acid and sulphides of copper and molybdenum were then removed by filtration. Ten ml of nitric acid was added to the filtrate, which was evaporated to a volume of about 5 ml. The solution was then diluted and the precipitations by zinc oxide made as usual.
[8] This mixture was analyzed to test the applicability of the method to the determination of cobalt in nickel-chromium resistance alloys.

If double precipitations by zinc oxide are made, the concentration of zinc chloride in the combined filtrates is materially increased, and the possibility of contamination of the precipitated cobalt by zinc must be considered. Two of the metallic residues (Nos. 6 and 10 in Table 2) were dissolved in hydrochloric acid and the cobalt reprecipitated by α-nitroso-β-naphthol. By igniting these precipitates, reducing in hydrogen, and weighing as cobalt metal, 4.81 and 4.82 per cent of cobalt were obtained, as compared with 4.82 and 4.84 per cent in the first precipitation. This shows that contemination by zinc is very slight and can usually be ignored.

IV. DETERMINATION OF MANGANESE

Table 3 shows the results obtained for manganese by precipitating with zinc oxide as described under cobalt and then determining manganese in the filtrates by the bismuthate method. Because chlorides interfere in this determination, the samples were dissolved in 25 ml of dilute sulphuric acid (1 : 5) and oxidized with nitric acid.

TABLE 3.—*Results for manganese obtained by the bismuthate method after single and double precipitations by zinc oxide*

No.	Material analyzed	Manganese present	Manganese found after single precipitation with ZnO	Error	Manganese found after double precipitation with ZnO	Error	Other elements added	Temperature of ZnO precipitation	Remarks
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*		
1	B. S. Cr-W-V steel No. 50a.[1]	0.287	0.278	−0.009	0.285	−0.002	.....	90° to 100° C.	
2	.....do.....	.287	.274	−.013	.283	−.004	.....	20° to 25° C.	
3	B. S. ingot iron No. 55.	.019	.021	+.002	.023	+.004	.....	90° to 100° C.	Determined manganese colorimetrically by the periodate method.
4	.....do.....	.019	.020	+.001	.024	+.005	.....	20° to 25° C.	
5	B.S.Cr-Ni(18-8) steel No. 101.[2]	.555	.544	−.011	.560	+.005	.....	90° to 100° C.	
6	.....do.....	.555	.540	−.015	.558	+.003	.....	20° to 25° C.	
7	B. S. Cr-Mosteel No. 72.[3]	.651	.650	−.001	.655	+.004	0.5 Cu..	90° to 100° C.	
8	.....do.....	.651	.650	−.001	.653	+.002	0.5 Cu..	20° to 25° C.	
9	B. S. ferrovanadium No. 61.[4]	3.57	3.55	−.02	.....	.....	.....	90° to 100° C.	
10	.....do.....	3.57	3.57	.00	3.60	+.003	.....	20° to 25° C.	

[1] See footnote 2 under Table 1.

[2] This steel has the following percentage composition: C, 0.06; Mn, 0.555; P, 0.014; S, 0.011; Si, 0.766; Cu, 0.054; Ni, 8.44; Cr, 17.53; V, 0.045; Mo, 0.005.

[3] This steel has the following percentage composition: C, 0.294; Mn, 0.651; P, 0.016; S, 0.021; Si, 0.137; Cu, 0.064; Ni, 0.288; Cr, 0.911.

[4] This sample has the following percentage composition: V, 31.15, C, 1.15; Fe, 52.8; Mn, 3.57; P, 0.243; Si, 7.78; Cu, 0.29; Ni, 1.33; Cr, 0.52; Mo, 0.72; Ti, 0.23.

V. BEHAVIOR OF OTHER CONSTITUENTS OF STEEL IN THE PRECIPITATION BY ZINC OXIDE

1. IRON

Ferric iron is completely precipitated. Precipitation of ferrous iron is incomplete.

2. NICKEL

Separation of iron is not necessary in determinations of nickel in steel, but a few tests were made to ascertain the behavior of nickel. By making single precipitations with zinc oxide, filtering and determining nickel in aliquot portions of the filtrates by the dimethylglyoxime method, 0.203, 1.13, and 8.03 per cent were obtained in steels containing 0.288, 1.21, and 8.44 per cent, respectively. By making double precipitations with zinc oxide, as described in the determination of cobalt, and examining the final precipitates containing the iron, chromium, etc., no nickel was detected in the case of the steel containing 0.288 per cent of nickel, 0.02 per cent was found in the case of the steel containing 1.21 per cent, and 0.10 per cent in the case of the steel containing 8.44 per cent. These tests indicate that nickel is retained in the bulky precipitate even if two precipitations by zinc oxide are made. If the percentage of nickel is low, the retention is negligible. Single precipitations do not yield satisfactory separations.

3. TUNGSTEN

If tungsten is oxidized to yellow tungstic acid before the addition of zinc oxide, none will be found in the filtrate. If it is not oxidized, a little will be found in the filtrate. This will contaminate cobalt if the cobalt is precipitated with α-nitroso-β-naphthol. If an excess of zinc oxide is added to an acid solution containing no other elements, such as iron, that are precipitated, a large proportion of the tungsten remains in solution. The amount remaining in solution varies, because more is precipitated if the time of digestion is increased.

4. VANADIUM

In a solution containing no other elements that are precipitated, quadrivalent vanadium is completely precipitated, whereas quinquevalent vanadium divides, at least one-half passing into the filtrate. Both quadrivalent and quinquevalent vanadium are completely precipitated if a tenfold excess of ferric iron is present. In the absence of ferric iron it is difficult to obtain a clear filtrate in the case of quadrivalent vanadium. Tests to ascertain the behavior of quinquevalent vanadium were made by adding ferrovanadium to ingot iron in such quantity that the mixtures contained 1 g of iron and 0.1 g of vanadium. These mixtures were dissolved, the iron and vanadium were oxidized, and the solutions treated with an excess of zinc oxide and filtered. Precipitations were made at 20° and at 90° C. The filtrates were acidified with sulphuric acid and treated with hydrogen peroxide. Less than 0.1 mg of vanadium was found in any case. Similar tests of ferrovanadium alone (53 per cent of Fe and 31 per cent of V) showed 0.1 mg of vanadium in the filtrates obtained by precipitating at 20° to 25° C. and 0.2 mg at 90° to 100° C.

5. CHROMIUM

Sexivalent chromium is not precipitated by zinc oxide; trivalent chromium is completely precipitated either in the presence or absence of iron.

6. COPPER AND MOLYBDENUM

Copper is almost completely precipitated in the absence of iron, but only about one-half of the molybdenum is precipitated under similar conditions. Copper to make 0.5 per cent was added to solutions of 1-g samples of ingot iron and of chrome-tungsten-vanadium steel, and double precipitations by zinc oxide were made. In six such tests the combined filtrates of each test showed from 0.2 to 0.5 mg of copper. Similar tests, but using 0.5 per cent of molybdenum instead of copper, showed that from 1 to 2 mg of molybdenum passed into the filtrate. Molybdenum and copper are precipitated by α-nitroso-β-naphthol, but during the ignition of cobalt to oxide at temperatures between 750° and 900° C. the former is partially volatilized. Consequently contamination by molybdenum under these conditions seldom exceeds 1 mg.

The retention of cobalt in the precipitate formed by zinc oxide is slightly greater if the material contains as much as 0.5 per cent of copper or molybdenum. The average of six determinations of cobalt in such precipitates showed this retention to be 0.2 mg greater

than was the case when copper and molybdenum were absent. Tests have shown that if the material contains less than 0.15 per cent of copper or molybdenum, it is safe to ignore the retention of cobalt in the precipitate formed by zinc oxide, and also the contamination of the cobalt by copper and molybdenum. The two errors tend to cancel each other.

7. URANIUM

Sexivalent uranium is completely precipitated in the presence of a tenfold excess of ferric iron. In the absence of ferric iron 0.5 mg and 0.6 mg of uranium oxide, U_3O_8, were found in the filtrates in two tests, involving 10 and 20 mg of uranium respectively. Quadrivalent uranium is completely precipitated in the absence of iron.

8. ZIRCONIUM AND TITANIUM

Zirconium and quadrivalent titanium are completely precipitated. Peroxidized titanium passes into the filtrate.

9. SILICON

Sodium silicate, equivalent to 0.02 g of silica, was added to 1 g of ingot iron, after which the iron was dissolved and oxidized. After making a precipitation with zinc oxide in the usual manner and filtering, the filtrate was tested for silica by dehydration with sulphuric acid. One milligram of silica was found.

10. ALUMINUM

Aluminum chloride, equivalent to 0.02 g of aluminum, was added to 1 g of ingot iron, after which the iron was dissolved and oxidized. A precipitation by zinc oxide was made in the usual manner, and the solution was filtered. No aluminum was found in the filtrate.

11. PHOSPHORUS, ARSENIC, ANTIMONY, TIN (LEAD)

Phosphorus (as orthophosphate) and tri and quinquevalent arsenic are quantitatively precipitated in the presence of a ten to twenty fold excess of ferric iron.

Trivalent antimony is almost completely precipitated in the presence of a ten to twenty fold excess of ferric iron. In tests involving 5 mg of antimony an average of only 0.3 mg was found in the filtrates. Quinquevalent antimony is not completely precipitated in the presence or absence of ferric iron.

Bivalent tin is not completely precipitated. Quadrivalent tin is completely precipitated in the presence or absence of ferric iron. Filtration is difficult if much tin is involved.

Lead divides, but by far the greater part remains in the precipitate.

Antimony, tin, and lead are precipitated by α-nitroso-β-naphthol and must be taken into consideration if this reagent is to be used.

VI. CONCLUSIONS

If a precipitation by zinc oxide is made in a solution of a steel obtained by dissolving the steel in hydrochloric or sulphuric acid and oxidizing with nitric acid, the precipitate will contain all of the

iron, tungsten, vanadium, chromium, uranium, zirconium, titanium, aluminum, phosphorus, arsenic, tin, and nearly all of the copper, molybdenum, and silicon. Ferrous iron, tungsten if not previously oxidized, and small quantities of silicon, copper, molybdenum, antimony, and lead may be expected in the filtrate if these were present in appreciable amounts.

Small amounts of sodium carbonate in the zinc oxide used in separating cobalt and manganese from iron, chromium, etc., are not objectionable if only a slight excess of reagent is added.

Separations of iron and certain other constituents of steel from cobalt and manganese by precipitating with zinc oxide are satisfactory if double precipitations are made. Results for cobalt tend to be low if only a single precipitation is made. Neither single nor double precipitations are entirely satisfactory for the separation of large amounts of nickel. The temperature at which precipitations by zinc oxide are made has very little influence on the results.

VII. ACKNOWLEDGMENT

Acknowledgment is made to Dr. G. E. F. Lundell, under whose direction this investigation was made.

WASHINGTON, September 16, 1931.

THE DECOMPOSITION OF TRICALCIUM SILICATE IN THE TEMPERATURE RANGE, 1,000° -1,300° C.

By E. T. Carlson

ABSTRACT

The decomposition of tricalcium silicate, $3CaO.SiO_2$, into dicalcium silicate and free lime, has been studied in the temperature region 1,000°–1,300° C. The extent of decomposition, measured by means of free-lime determinations, was found to be greatest at about 1,175° C. After a day's heating at this temperature the decomposition was about fifteen times as great as after a day's heating at 1,000° C. Above 1,175° the rate decreased rapidly, and the amount of free lime was negligible at 1,300°. The decomposition appears to be autocatalytic, the rate of the reaction being increased by the presence of either of the decomposition products, dicalcium silicate and lime. Exposure of tricalcium silicate to moist air promotes the decomposition because of the action of the moisture on the silicate, liberating lime. Freshly burned tricalcium silicate, containing a minimum amount of free lime, decomposes very slowly. The presence of gypsum accelerates the decomposition, probably because of the formation of free lime by dissociation of the gypsum.

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I. INTRODUCTION

It has long been known that the prolonged calcination of Portland cement results in a product having hydraulic properties inferior to those of a rapidly burned cement. An explanation of this phenomenon was given by E. Leduc [1] in 1901, following some experiments on the liberation of lime from cements on calcination at 1,000° [2] for various periods of time. The lime liberated, determined by dissolving it out of the cement with sugar solution, was found to increase with the length of time of heating, reaching a maximum at 48 hours. Leduc attributed the unsoundness of these cements to the free lime present.

The more recent work of S. L. Meyers [3] showed that freshly burned cements break down much less readily than those which have been

[1] E. Leduc, Notes on the Dissociation of Hydraulic Products, Internat. Assn. for Testing Materials, vol. 3, 1901.

[2] All temperatures are expressed in degrees centigrade.

[3] S. L. Meyers, Breaking Down of Tricalcium Silicate by Heat, Rock Products, vol. 33, No. 8, pp. 78–79, 1930.

aged for some time. Meyers also experimented with the compounds $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$, the chief constituents of Portland cement. Of these, only the first was found to liberate lime on heating. These results were confirmed by W. Lerch.[4]

The present study was undertaken in order to determine the conditions affecting the decomposition of tricalcium silicate.

II. EXPERIMENTAL WORK

1. PREPARATION OF MATERIAL

Sample No. 1 was prepared according to the method repeatedly described in previous publications of this Bureau.[5] A petrographic examination of the product showed that it consisisted almost entirely of tricalcium silicate, with a trace of dicalcium silicate. The free-lime content, as determined by the ammonium acetate method, was 0.35 per cent. The material was kept in a glass-stoppered bottle.

Samples Nos. 2, 3, 4, and 5 were prepared in substantially the same manner. Nos. 2 and 3 were burned several months before this study was begun, and Nos. 4 and 5 were about three years old. Petrographic examination revealed the fact that the grains of these samples has been altered superficially, giving them a mottled appearance, this being more noticeable in the older samples. The altered surface layer was too thin to permit a determination of its optical properties. Since these samples had been kept in loosely stoppered bottles, it was assumed that the alteration was due to the action of moisture or carbon dioxide in the air.

2. METHOD OF DETERMINING EXTENT OF DECOMPOSITION

A sample of the silicate (1 or 2 g) was placed in a platinum thimble, which was suspended in a platinum resistance furnace and heated for a definite length of time, the temperature being kept constant to within $\pm 10°$. Due to fluctuations in the line voltage, closer temperature control was impossible when samples were left in the furnace over night. Temperatures were measured by means of a platinum—platinum-rhodium thermocouple and a potentiometer. After removal from the furnace, the sample was allowed to cool in air, and the free lime was determined at once by the ammonium acetate method.[6] In the later experiments this method was modified by the substitution of phenol red for phenolphthalein as indicator, the former being more satisfactory because it does not fade in alcoholic solution.

3. EFFECT OF AGE OF SAMPLE

As mentioned above, previous investigators have shown that the amount of lime liberated on heating a cement is dependent to some extent on the age of the sample. That this is also true of tricalcium silicate is shown in Table 1, which gives a comparison of the various samples used in this study.

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[4] Unpublished report.

[5] Hansen, Further Studies on Portland Cement Compounds by the X-ray Diffraction Method, J. Am. Ceram. Soc., vol. 11, No. 2, pp. 68-78, 1928.

[6] Lerch and Bogue, Revised Procedure for the Determination of Uncombined Lime in Portland Cement, Ind. Eng. Chem., Anal, ed., vol. 2, p. 296, 1930.

TABLE 1.—*Effect of age of sample on the decomposition of tricalcium silicate by heat*

Sample No.	Age of sample	Temperature	Time of heating	Free CaO before heating	Free CaO after heating
		°C.	Hours	Per cent	Per cent
1	1 day	1,150	23	0.4	1.0
2	About 1 year	1,175	23	.0	14.1
3	Several months	1,150	23	.2	15.2
4	3 years	1,150	23	.0	17.5
5	do	1,150	23	.0	18.2

It will be seen that the tendency to dissociate is much less in the case of the fresh material. In view of this fact, it was thought that perhaps the stability of the old samples could be renewed by heating them to higher temperatures. Table 2 gives the results of some experiments which showed this to be the case.

TABLE 2.—*Effect of preliminary heating at higher temperatures*

Sample No.	Heat treatment	Free CaO after heating
		Per cent
2	Held 23 hours at 1,175° C. (Table 1)	14.1
2	Heated to 1,450°; cooled to 1,150° and held 24 hours	3.9
2	Held 17 hours at 1,325°; cooled to 1,175° and held 24 hours	.85
2	Held 3 hours at 1,400°; cooled to 1,175° and held 17 hours	.27
2	Held 3 hours at 1,400°; cooled to room temperature; held 17 hours at 1,175°	.10

It is evident that the condition responsible for the rapid breakdown of the silicate may be removed by prolonged heating at temperatures of 1,325° C. or higher.

4. EFFECT OF TEMPERATURE

In order to determine the temperature at which the amount of decomposition reached a maximum, samples of the silicate were held at various temperatures (±10°) for 23 hours, and then cooled quickly and tested for free lime. The 23-hour heating period was chosen merely for convenience, as this made it possible to make a determination every day. Table 3 gives the results obtained.

TABLE 3.—*Decomposition of $3CaO.SiO_2$ on heating for 23 hours at various temperatures*

Temperature [1] (±10°)	Free CaO after heating		Temperature [1] (±10°)	Free CaO after heating	
	Sample No. 2	Sample No. 3		Sample No. 2	Sample No. 3
°C.	Per cent	Per cent	°C.	Per cent	Per cent
1,000	----------	1.3	1,200	14.9	----------
1,050	----------	2.1	1,225	----------	12.2
1,075	6.6	----------	1,250	8.1	10.6
1,100	----------	11.0	1,275	1.6	----------
1,125	12.3	----------	1,300	----------	.2
1,150	----------	15.2	1,325	.16	----------
1,175	14.1	14.4	1,350	.00	----------

[1] The temperatures for sample No. 2 were measured with a millivoltmeter, possibly introducing a slight error.

These values are plotted in Figure 1. It should be borne in mind that the points do not represent equilibrium conditions, but merely the extent to which the reaction had progressed in 23 hours, consequently the scattering of the points is not surprising. In view of this fact the single curve drawn probably approximates the correct curve for both samples. It will be seen that the amount decomposed attains a maximum at about 1,175°.

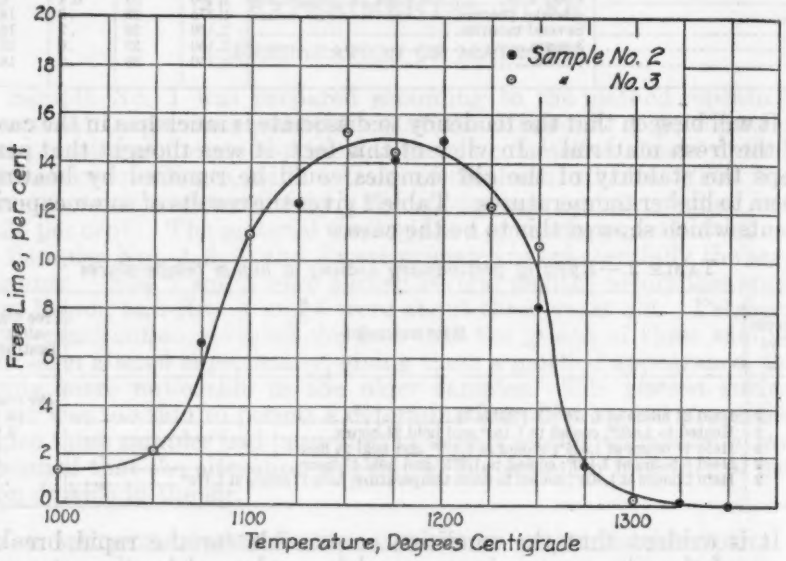

FIGURE 1.—*Decomposition of tricalcium silicate on heating for 23 hours at various temperatures*

5. INCREASE IN DECOMPOSITION WITH TIME OF HEATING

Table 4 and Figure 2 show the change in the extent of the decomposition with time at three different temperatures. Sample No. 4 was used for these experiments.

TABLE 4.—*Amount of decomposition of $3CaO.SiO_2$ at different temperatures*

Temperature (±10°)	Length of heating	Free CaO	Temperature	Length of heating	Free CaO
°C.	*Hours*	*Per cent*	*°C.*	*Hours*	*Per cent*
1,150	1	4.7	1,200	16	11.3
1,150	2	6.2	1,250	1	.9
1,150	3	7.8	1,250	2	1.2
1,150	7	11.6	1,250	5	1.8
1,150	17	15.2	1,250	16	3.8
1,150	23	17.5	1,250	23	10.6
1,150	53	18.9	1,250	24	2.7
1,200	1	3.2	1,250	25	8.7
1,200	2	4.4	1,250	48	5.8

It will be noted that the results obtained on heating the samples to 1,250° are decidedly inconsistent, although at 1,150° the points lie very nearly on a smooth curve. This is perhaps to be expected, since the rate of the reaction decreases rapidly with increase in tem-

perature in the region of 1,250°. As can readily be seen from Figure 1, a difference of ± 10° in temperature could account for wide variations in the amount of decomposition. Such changes of temperature were unavoidable when the samples were left in the furnace overnight, due to fluctuations in the line voltage.

From the shape of the curves it appears that the free CaO content approaches a maximum value which is different for different temperatures. The theoretical amount of free CaO calculated from the equation

$$3CaO.SiO_2 \rightarrow 2CaO.SiO_2 + CaO$$

on the assumption that it goes to completion, is 24.57 per cent, which is considerably in excess of any of the experimental values obtained.

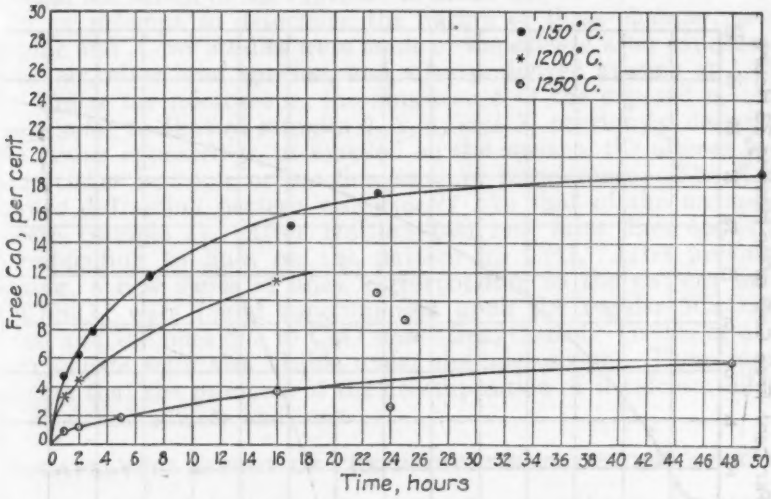

FIGURE 2.—*Increase in decomposition of tricalcium silicate with time of heating*

6. EFFECT OF MOISTURE

Since it was evident that the stability of $3CaO.SiO_2$ is affected by exposure to air, it was decided to ascertain, if possible, any existing quantitative relation between the ignition loss of the material and its decomposition by heat. The action of the air was accelerated by placing some of the silicate (sample No. 1) in an evaporating dish, which was then placed in a larger dish containing a little water and covered with a watch glass. In this way the material was exposed to a rather humid atmosphere. No attempt was made to exclude carbon dioxide. Samples were removed from time to time, and the loss on ignition determined, after which they were heated for 23 hours at 1,150° and tested for free lime. The results are shown in Table 5 and Figure 3.

TABLE 5.—*Decomposition of $3CaO.SiO_2$ as a function of the ignition loss*

Ignition loss	Free CaO after heating	Ignition loss	Free CaO after heating	Ignition loss	Free CaO after heating
Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
0.23	0.6	0.60	2.2	2.52	11.4
.41	1.2	.73	3.5	5.02	14.4
.47	1.5	1.34	6.1	7.00	16.8
.51	2.6	1.70	8.8		
.54	2.2	1.96	8.0		

It is evident from these data that moisture has a great effect on the stability of tricalcium silicate. Although the products of the hydration of tricalcium silicate on the addition of water are not yet known

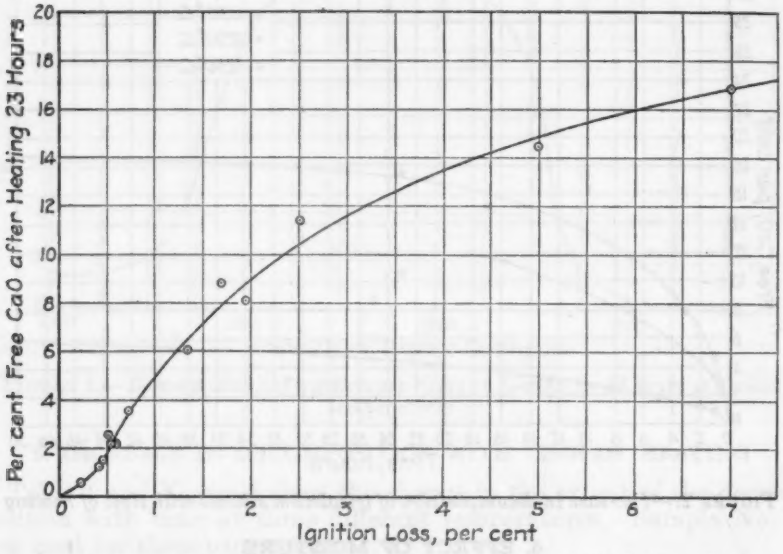

FIGURE 3.—*Effect of moisture on the decomposition of tricalcium silicate*

with certainty, it is known that calcium hydroxide is formed and that a gelatinous substance remains, which is very probably a hydrated calcium silicate.

Both calcium carbonate and hydrated silica decompose quite rapidly at 1,100° C.; hence it was argued that ignition of the exposed silicate for 20 minutes over a Fisher burner (Meker type) would remove all but traces of water and carbon dioxide, at the same time liberating the lime which was present as either the hydroxide or the carbonate. Two samples of the silicate were exposed to moist air for different lengths of time, then ignited for 20 minutes over a Fisher burner. After the ignition loss was determined, the samples were tested for free lime without further heating, while a portion was held at 1,150° for 23 hours and then tested. The results are given in Table 6.

TABLE 6.—*Lime liberated on ignition of exposed tricalcium silicate*

Ignition loss	Free CaO after ignition	Free CaO after heating 23 hours at 1,150° C.
Per cent	*Per cent*	*Per cent*
4.64	4.5	[1] 14.0
5.02	3.1	14.4

[1] Estimated from Figure 3.

The data clearly show that the amount of lime liberated on heating for 23 hours is much greater than that produced by a hydroxide through the action of the exposure to moist air.

In an attempt to determine the nature of these changes, petrographic and X-ray studies were made of the silicate after exposure to moist air, after brief ignition, and after prolonged heating at 1,150° C. Under the microscope, the appearance of the exposed material was similar to that of samples 2, 3, 4, and 5, previously described. The grains appeared to be mottled on the surface, the altered layer being either isotropic or too thin to show interference. The X-ray powder diffraction pattern was exactly like that of the unexposed silicate (sample 1). After ignition two new faint lines appeared, corresponding to lines on the pattern for CaO. After prolonged heating, a new series of lines, corresponding to the pattern for β-$2CaO.SiO_2$, were found superimposed upon the regular $3CaO.SiO_2$ series, and the lines due to CaO were strengthened. Grains of dicalcium silicate were also visible under the microscope. These results indicate that the products of the decomposition of tricalcium silicate are dicalcium silicate and lime.

7. CATALYTIC EFFECT OF THE PRODUCTS OF DECOMPOSITION

It is evident that the extent of the decomposition on prolonged heating is much greater than can be accounted for on the assumption that all the free lime comes from the calcium hydroxide or calcium carbonate which has been formed by the action of the air.

In order to determine the effect of free CaO on the stability of the silicate, portions of sample 1 were thoroughly mixed with small amounts of CaO or $Ca(OH)_2$, and the free lime determined after 23 hours' heating at 1,150° C. In all cases there was a marked increase in the free-lime content, indicating that the presence of CaO accelerates the decomposition. Since CaO has this effect, it might be expected that the other product of the decomposition, dicalcium silicate, would act in a similar manner. Experiments showed that this was indeed the case. Five per cent of gamma dicalcium silicate mixed with a portion of tricalcium silicate (sample 1) caused it to decompose, yielding 5.8 per cent free CaO after 23 hours' heating at 1,150°. It should be noted that the gamma form of dicalcium silicate inverts to the beta modification far below the temperature used, so the latter was the form in contact with the tricalcium silicate.

These results were verified by experiments on sample 4. As this was one of the "weathered" samples, it was first renewed by heating to 1,425° C. The data obtained are shown in Table 7.

TABLE 7.—*Effect of presence of CaO and $2CaO.SiO_2$ on the decomposition of $3CaO.SiO_2$*

Sample No.	Material added	Temperature	Time of heating	Free CaO after heating	Free CaO in excess of that added
		°C.	Hours	Per cent	Per cent
1	None	1,150	23	0.4	0.4
1	10 per cent CaO	1,150	23	15.3	5.3
1	5 per cent CaO	1,150	23	11.5	6.5
1	$Ca(OH)_2$ equivalent to 5 per cent CaO	1,150	23	12.9	7.9
1	2 per cent CaO	1,150	23	6.8	4.8
1	5 per cent $2CaO.SiO_2$	1,150	23	5.8	5.8
4 [1]	None	1,150	23	1.4	1.4
4 [1]	5 per cent CaO	1,150	23	15.3	10.3
4 [1]	5 per cent $2CaO.SiO_2$	1,150	23	7.1	7.1

[1] Renewed.

8. CATALYTIC EFFECT OF GYPSUM

Although Meyers stated that the presence or absence of gypsum in cement had no effect on the liberation of lime, the later work of Mullan [7] seems to indicate that gypsum tends to accelerate the reaction.

In the present study, samples of tricalcium silicate were mixed with small amounts of gypsum and heated in the manner previously described. In all cases the liberation of lime was very marked. It was thought that this might be due to the decomposition of the calcium sulfate and the catalytic effect of the lime liberated. Accordingly, a sample of gypsum was heated in the same manner and tested for free lime, but the decomposition was found to be rather slight. However, it is possible that this reaction proceeds more rapidly in the presence of tricalcium silicate. A mixture of the two substances showed a decrease in the SO_3 content after heating, indicating that this is actually the case. In this connection it is interesting to note that other investigators have found the decomposition temperature of calcium sulfate to be lowered by the presence of silica. Cobb [8] states that the decomposition of $CaSO_4$ becomes appreciable at 1,225°–1,230° normally, but starts at 1,005°–1,010° when the sulfate is mixed with SiO_2.

It should be noted, however, that the presence of gypsum is not essential to the process of decomposition, as the samples previously described were shown by analysis to be free of SO_3.

The above results are summarized in Table 8.

TABLE 8.—*Effect of gypsum on the decomposition of tricalcium silicate*

Sample No.	Material added	Temperature	Time of heating	Free CaO after heating	SO_3 after heating	SO_3 lost
		°C.	Hours	Per cent	Per cent	Per cent
1	5 per cent gypsum	1,150	23	10.0		
1	do	1,150	23		1.87	0.46
1	5 per cent anhydrite	1,150	23	11.4		
4 (renewed)	5 per cent gypsum	1,150	23	17.5		
(None)	Gypsum alone	1,150	23	.32		

[7] T. F. Mullan, Effect of gypsum on the decomposition of tricalcium silicate by heat, Rock Products, vol. 33, No. 18, pp. 62–63, 1930.

[8] J. W. Cobb, The synthesis of a glaze, glass, or other complex silicate, J. Soc. Chem. Ind., vol. 29, pp. 69–74, 1910.

III. DISCUSSION

From the foregoing results it is possible to obtain some insight into the mechanism of the decomposition. It seems evident that tricalcium silicate is in a metastable state at temperatures below 1,300°. It is known that between 1,400° and 1,900° the reaction

$$2CaO.SiO_2 + CaO \rightarrow 3CaO.SiO_2$$

takes place, though it proceeds rather slowly at 1,400°. This, in fact, is the method used in preparing tricalcium silicate. It has been shown by Rankin[9] that at temperatures above 1,900° the reaction proceeds in the opposite direction. The results of the above experiments indicate that the reaction also tends to proceed in the reverse direction at temperatures below 1,300°, but that the presence of at least one of the products of the reaction is necessary to start the decomposition. It is probable that the reaction takes place only at points of contact between particles of tricalcium silicate and one of the other two phases. A reaction of this type would be analogous to the crystallization from a supercooled liquid on "seeding," but it must be remembered that in the case under consideration all three phases are solid, and the reaction is necessarily slow. As even the purest samples prepared contained traces of CaO and $2CaO.SiO_2$, these particles naturally acted as centers of reaction, resulting in a slight decomposition. When either of the two products was thoroughly mixed with the tricalcium silicate, the centers of the reaction were much more numerous, resulting in a greater rate of decomposition.

If this explanation is accepted, the rôle of "aging" becomes clear. The moisture of the air reacts with the silicate, liberating hydrated lime, which soon carbonates. When the material is then heated, CaO is obtained, and the grains of this material catalyze the further decomposition of the silicate. It is possible that $2CaO.SiO_2$ is also formed when the "aged" silicate is heated, and that this also has a catalytic effect. If this material is then heated to 1,400°C., the dicalcium silicate and lime, already in close contact, reunite to form tricalcium silicate, which then shows the characteristics of the freshly prepared material.

From the curves in Figure 2 it seems probable that the decomposition reaches a maximum value which varies with temperature. At 1,175° the tendency to dissociate reaches a maximum, while at 1,300° and above, the tendency for the lime and dicalcium silicate to recombine is predominant. The existence of any definite equilibrium has not been determined, since to do so would require the maintenance of constant temperatures very accurately over a period of several days, perhaps weeks, especially at temperatures below 1,150°. It should be noted that the curves in Figure 1 do not necessarily indicate a tendency toward recombination at temperatures below 1,150°. The falling off of the curves at these lower temperatures is more probably due to a slower speed of reaction.

Although the rôle of gypsum as a catalyst for the reaction has not been definitely established in this study, it seems probable that its action is caused by the lime liberated from the calcium sulfate on heating.

[9] Rankin and Wright, The Ternary System $CaO—Al_2O_3—SiO_2$, Am. J. Sci., vol. 39, pp. 1–79, 1915.

The writer is indebted to P. H. Bates and L. S. Wells for their many helpful suggestions and to H. Insley for his assistance with the petrographic and X-ray study.

IV. SUMMARY

1. Tricalcium silicate tends to dissociate into dicalcium silicate and lime when heated to temperatures between 1,000° and 1,300° C.

2. The amount of decomposition reaches a maximum at about 1,175°, being about fifteen times as great at this temperature as at 1,000°, after a day's heating.

3. The reaction is accelerated by the presence of either of the products of decomposition, namely, dicalcium silicate or free lime.

4. Tricalcium silicate which has been exposed to moist air decomposes much more readily than when freshly burned, probably due to the presence of lime liberated by the action of moisture on the silicate.

5. The presence of gypsum also accelerates the decomposition. This may be due to lime liberated by dissociation of the gypsum.

WASHINGTON, August 24, 1931.

THE DETERMINATION OF THE COEFFICIENT OF CUBICAL EXPANSION OF SOLID BENZOIC ACID BY MEANS OF A GAS-FILLED DILATOMETER

By E. R. Smith

ABSTRACT

By measurement with a constant-volume gas-filled dilatometer the coefficient of expansion of benzoic acid between 15° and 30° C. was found to be 0.00052 per degree C.

For use in another investigation it was necessary to know the coefficient of cubical expansion of benzoic acid at room temperatures. Since no determinations of this quantity could be found in the literature, measurements were made from 15° to 30° C.

The method employed consisted in measuring the pressure at different temperatures of a definite amount of dry air inclosed in a flask with a relatively large quantity of prefused benzoic acid, keeping the total volume of the system constant.

The apparatus is shown in Figure 1. Benzoic acid (Bureau of Standards Standard Sample No. 39d) was melted in a weighed and calibrated quartz flask, *A*, immersed in a bath of liquid petrolatum at 140° C. After a suitable amount of the acid had been introduced and melted in the flask, the latter was taken out of the heating bath, cleaned, and allowed to cool in a desiccator. On solidifying, the mass of benzoic acid developed numerous cracks and separated from the flask. When cool, the flask was stoppered and reweighed to obtain the weight of the sample. A current of air, dried and freed from carbon dioxide by passing through concentrated sulphuric acid, sodium hydroxide on asbestos, and magnesium perchlorate trihydrate, in the order named, was then blown into the neck of the flask for a few minutes. Then the lubricated ground Pyrex capillary stopper *B*, which was sealed to the volume-regulating manometer *C* and the pressure-regulating manometer *E*, was inserted. The apparatus was next placed in a water thermostat having a plate-glass front and back and provided with a heater, cooling coil, stirrer, and a mercury regulator, the latter connected with a vibrator and the electron

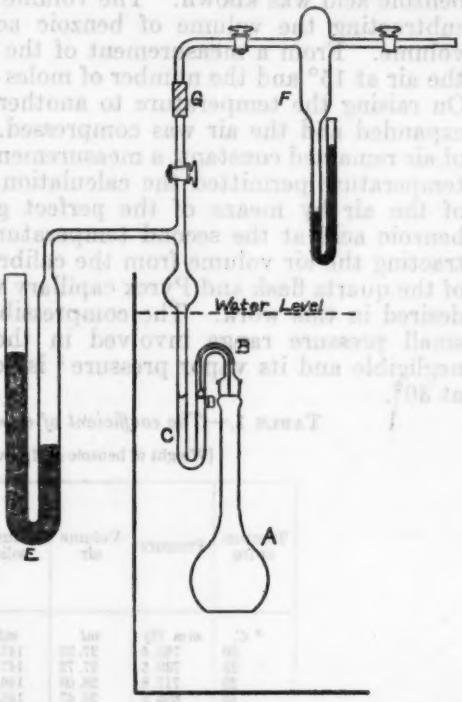

FIGURE 1.—*Apparatus for measuring coefficients of expansion*

tube circuit described by Beaver and Beaver.[1] The extreme variations in temperature at a given setting were less than 0.01°. The absolute value of the temperature was measured to 0.1°. The volume of the flask, capillary, and tube to the mark D had been previously determined by calibration. Manometer C contained butyl phthalate and manometer E contained mercury. The tube F was connected to the apparatus by means of rubber tubing at G. The purpose of F was to regulate the pressure so as always to bring the meniscus of the butyl phthalate to the mark D before taking a measurement, and thus have the total volume of the system equal to the calibrated volume. Butyl phthalate was found to be advantageous for this purpose because of its low vapor pressure and density.

From the weight of benzoic acid and its density,[2] the volume of benzoic acid was known. The volume of air at 15° was obtained by subtracting the volume of benzoic acid from the total calibrated volume. From a measurement of the pressure, the PV product for the air at 15° and the number of moles of air present were calculated. On raising the temperature to another fixed value the benzoic acid expanded and the air was compressed. Since the number of moles of air remained constant, a measurement of the pressure at the second temperature permitted the calculation of the corresponding volume of the air by means of the perfect gas law. The volume of the benzoic acid at the second temperature was then obtained by subtracting the air volume from the calibrated volume. The expansion of the quartz flask and Pyrex capillary was negligible for the accuracy desired in this work. The compressibility of benzoic acid over the small pressure range involved in the measurements is obviously negligible and its vapor pressure[3] is considerably less than 0.1 mm at 30°.

TABLE 1.—*The coefficient of expansion of benzoic acid*

[Weight of benzoic acid in vacuo 185.27 g]

Temperature	Pressure	Volume air	Volume solid	γ	Volume solid, calculated from average
° *C.*	*mm Hg*	*ml*	*ml*		
30	762.5	27.33	147.48		
25	739.5	27.72	147.09	0.000523	147.1
20	717.8	28.08	146.73		146.7
15	695.8	28.47	146.34		
20	716.9	28.11	146.70		146.7
25	739.0	27.74	147.07	0.000514	147.1
30	761.9	27.35	147.46		

Average γ, 0.00052.

The results of one series of measurements are shown in Table 1. After taking measurements at successively lower intervals of 5° between 30° and 15°, the process was reversed by raising the temperature by 5° intervals from 15° to 30° in order to approach the equilibrium from both sides. The coefficient γ was calculated by means of the equation $V_t = V_o(1+\gamma t)$ in which V_t is the volume of

[1] Beaver and Beaver, J. Ind. Eng. Chem., vol. 15, p. 359; 1923.
[2] 1.266 at 15° C. Int. Crit. Tables, vol. 1, p. 208.
[3] Int. Crit. Tables, vol. 3, p. 208.

any given weight of benzoic acid at the centigrade temperature t, V_0 is its volume at 0° C. and γ is the coefficient of cubical expansion, $\frac{1}{V_0}\left(\frac{\Delta V}{\Delta t}\right)$. The average value of γ between 15° and 30° was found to be 0.00052 per degree C. The linearity of the expansion and the precision of the results can be seen from the last column of the table in which the volume of the benzoic acid as calculated from the average value of γ is given for comparison with the measured volume.

The author desires to express appreciation to E. W. Washburn, chief of the chemistry division of this bureau, for suggesting the method of measurement.

WASHINGTON, September 30, 1931.

ISOLATION OF NORMAL NONANE FROM A MIDCONTINENT PETROLEUM [1]

By Joseph D. White [2] and F. W. Rose, jr.[2]

ABSTRACT

An account is given of the separation of *n*-nonane in a high state of purity from a midcontinent petroleum by alternating fractional distillation and fractional crystallization. The density, refractive index, boiling point, freezing point, and infra-red absorption spectrum of the product are given and compared with the same properties of synthetic *n*-nonane. It is concluded that the petroleum under investigation contains about 1 per cent of *n*-nonane by weight.

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I. INTRODUCTION

The presence of *n*-nonane in American petroleum has been reported by several investigators.[3] The evidence given for its isolation is, however, not conclusive, except for the sample of very pure nonane obtained by Shepard, Henne, and Midgley with the aid of the chlorosulfonic acid process. The present paper describes the isolation of *n*-nonane from an Oklahoma petroleum.[4] Separation of this hydrocarbon in a high state of purity was accomplished by alternating fractional distillation and fractional crystallization.

II. INITIAL DISTILLATION

Approximately 600 gallons (2,300 liters) of the crude petroleum, which had been fractionated in a semicommercial still into 20-liter cuts,[5] was distilled thrice through a 20-plate bubbling-cap column of steel [6] in an atmosphere of carbon dioxide. The distillate collected at the rate of 500 ml an hour and was separated into cuts each having

[1] This paper describes some of the results obtained in an investigation on the separation, identification, and determination of the chemical constituents of commercial petroleum fractions listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the central petroleum committee of the National Research Council.

[2] American Petroleum Institute research associate.

[3] C. M. Warren, Proc. Am. Acad. Arts Sci., vol. 27, p. 80, 1891, communicated May 12, 1868; C. F. Mabery, Proc. Am. Acad. Arts Sci., vol. 31, pp. 33, 57, 1895; G. G. Brown and A. R. Carr, Ind. Eng. Chem., vol. 18, p. 722, 1926; A. F. Shepard and A. L. Henne, Ind. Eng. Chem., vol. 22, p. 356, 1930; A. F. Shepard, A. L. Henne, and T. Midgley, jr., J. Am. Chem. Soc., vol. 53, p. 1948, 1931.

[4] For further description and properties see E. W. Washburn, B. S. Jour. Research, vol. 2, p. 469, 1929.

[5] See J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 607, 1931.

[6] J. H. Bruun and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 470, 1929.

a 2° to 3° boiling range. Under the direction of S. T. Schicktanz,[7] the fractions boiling within the range 130° to 160° C. and having a total volume of approximately 175 liters were subjected to further fractionation in the 30-plate glass stills described in another publication.[8] The material was distilled with a reflux ratio of about 10:1 and the distillate was collected at the rate of 1 ml per minute in 1° cuts. A slow stream of dry carbon dioxide was bubbled continuously into the still pot throughout the distillation to minimize cracking and to prevent oxidation.

III. FRACTIONAL CRYSTALLIZATION

The initial freezing points of a certain few of the distillation fractions shown in Figure 1 are displayed in Figure 2. These fractions were subjected to a systematic fractional crystallization by a process

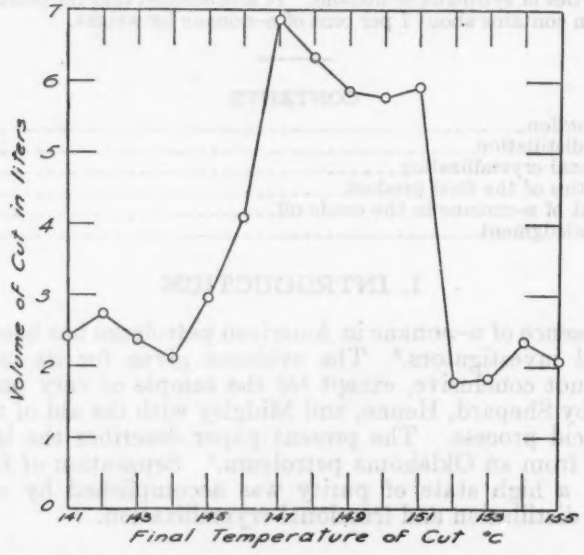

FIGURE 1.—*Distribution of volume of the fractions over the boiling range after two distillations through the glass stills*

of equilibrium melting previously described.[9] Cuts were made in accordance with the refractive index and those for which $n_D^{20} > 1.416$ were subjected to further distillation. Systematic fractionation, made in this manner by alternating crystallization and distillation as required, yielded finally about 18 liters of material with a refractive index of $n_D^{20} = 1.416$ or less, which after further crystallization gave about 10 liters of nonane, $n_D^{20} = 1.407$, as compared with 1.405, which is the value given for *n*-nonane in International Critical Tables.[10]

This approximately pure material was then distilled through a 35-foot column packed with jack chain,[11] under a pressure of 215 mm.

[7] American Petroleum Institute research associate.
[8] J. H. Braun and S. T. Schicktanz, B. S. Jour. Research, vol. 7, p. 851, 1931.
[9] R. T. Leslie and S. T. Schicktanz, B. S. Jour. Research, vol. 6, p. 381, 1931.
[10] Int. Crit. Tables, I, p. 230, 276, McGraw Hill Book Co., 8 1926.
[11] See footnote 8.

A large reflux ratio was maintained and the distillate collected at the rate of 1 ml per minute. The first 10 per cent distilled within 0.3° C. of the boiling point of *n*-nonane and possessed a refractive index from one to two units in the third decimal place higher than that of pure nonane. The remainder distilled (within a tenth of a degree) at exactly the temperature at which *n*-nonane possesses a vapor pressure of 215 mm. The refractive index of the distillate agreed, to one unit in the third decimal place, with that of pure nonane. The residue in the still pot, comprising about 10 per cent of the original charge, had a higher refractive index than that of *n*-nonane but slightly less than that of the first 10 per cent distilled.

From this distillation about 9 liters of nearly pure *n*-nonane were obtained in five lots, listed in Table 1 as Lots I to V. These lots represent the major portion of *n*-nonane obtained in the present investigation.

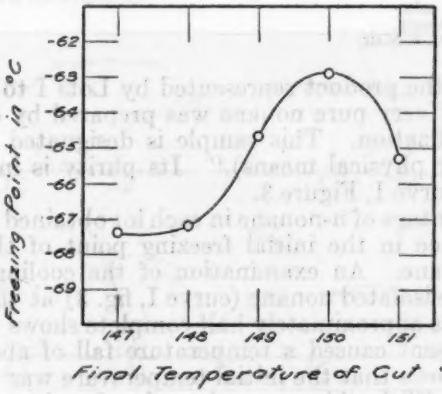

FIGURE 2.—*Variation in initial freezing point of the fractions with the boiling range*

IV. PROPERTIES OF THE FINAL PRODUCT

In Table 1 the physical properties of the product are compared with those of synthetic *n*-nonane,[12] and with those given by Shepard, Henne, and Midgley[13] for *n*-nonane isolated from petroleum. Densities were determined by E. E. Hill, of the weights and measures division, and refractive indices were measured by L. W. Tilton, of the optics division of this bureau.

Boiling points were determined in a modified McCoy boiling-point apparatus. In each case the thermometer was supported above the liquid in the inner tube. Unless otherwise specified, a 25-ohm platinum resistance thermometer was used.

[12] Prepared in this bureau by B. J. Mair.
[13] See footnote 3, p. 907.

TABLE 1.—*Comparison of the properties of n-nonane obtained from petroleum with the properties of synthetic n-nonane*

Material	Volume	d_D^{20} ±0.00003	n_D^{20} ±0.0001	Boiling point 760 mm Hg	Initial freezing point	Mole per cent n-nonane
	ml			°C.	°C.	
Lot I	2,000	----------	1.4041	[a] 150.5	[b] −54.4	95.8
Lot II	2,000	----------	1.4042	[a] 150.6	[b] −54.5	95.4
Lot III	2,000	----------	1.4042	[a] 150.6	[b] −54.5	95.4
Lot IV	2,000	----------	1.4043	[a] 150.6	[b] −54.6	94.9
Lot V	600	----------	1.4035	[a] 150.7	[b] −53.9	98.7
Best sample (by physical means)	75	0.71793	1.4033 [c]	[a] 150.73 ±0.01	[a] −53.65	99.9
Best sample (by chlorosulfonic acid)	73	.71803	1.4034 [c]	[a] 150.72 ±0.01	[a] −53.76	99.2
Shepard, Henne, and Midgley	----------	.71780	1.4034 [c]	150.71 ±0.01	−53.68	----------
Synthetic n-nonane	----------	.71770	1.4033 [c]	[a] 150.72 ±0.01	[a] −53.70	----------

[a] Relative boiling points only.
[b] Relative freezing points only.
[c] Values determined by B. J. Mair.

In addition to the product represented by Lots I to V in Table 1, a small sample of very pure nonane was prepared by continuing the fractional crystallization. This sample is designated in Table 1 as "best sample (by physical means)." Its purity is indicated by its freezing curve—curve I, Figure 3.

The mole percentage of *n*-nonane in each lot obtained was calculated from the difference in the initial freezing point of the sample and that of pure nonane. An examination of the cooling curve of the best sample of the isolated nonane (curve I, fig. 3) at the point where crystallization was approximately half complete shows that the traces of impurities present caused a temperature fall of about 0.015° C.; from which it follows that the initial temperature was too low by the same amount.[14] With this correction the freezing point of pure *n*-nonane becomes −53.63° C. This value was used for the purpose of calculating the purity of the different lots. For the heat of fusion of *n*-nonane the value calculated by Parks and Todd [15] was used.

One other portion from Lots I to V was treated with chlorosulfonic acid. It has been shown [16] that this acid readily attacks all side-chain hydrocarbons as well as aromatic and unsaturated ones, but only slowly attacks normal and unsubstituted naphthenic hydrocarbons. A mixture of 500 ml of Lot I and 200 ml of the acid was stirred constantly for 18 hours, after which the acid layer was removed, a fresh portion of acid added, and the treatment continued for another 18 hours. At the end of this time all action had apparently ceased. After separating the oil and acid layers the oil was washed with water to free it from acid and then with two separate portions of dilute potassium hydroxide. It was then washed again, dried over "Dehydrite," and fractionally distilled through the tall jack-chain column mentioned above.[17] The properties of the middle 75 ml fraction of the 428 ml distilled are recorded in Table 1

[14] W. P. White, J. Phys. Chem., vol. 24, p. 393, 1920.
[15] G. S. Parks and S. S. Todd, Ind. Eng. Chem., vol. 21, p. 1235, 1929.
[16] See footnote 3, p. 907; Shepard and Henne.
[17] In the particular instance at hand, fractional distillation would not be effective in separating n-nonane from a small amount of eyclooctane, if the latter were present, since the boiling points of the two compounds are almost identical. Upon distilling, however, all high-boiling material formed by the chlorosulfonic acid would be retained in the still pot.

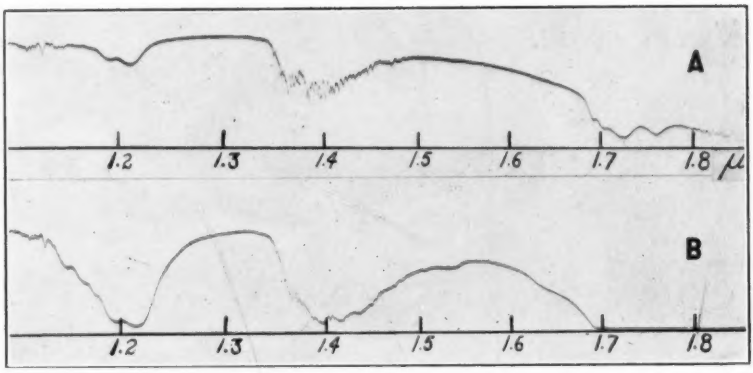

FIGURE 4.—*Infra-red absorption spectra of n-nonane*

Curves A and B are the automatically recorded energy transmission curves of the emission from a tungsten filament lamp through 1 mm and 1 cm cells, respectively, of normal nonane. The bands at 1.72 μ and 1.20 μ are the second and third harmonics, respectively, of the fundamental band at 3.43 μ which is observed in the absorption spectra of all hydrocarbons and is attributed to the H to C vibration. Absorption in the region of 1.4 μ is due to the combination frequency of the fundamentals at 3.43 μ and 6.86 μ. The curves show a resolving power of about 10 A to the slit width.

as those of "best sample (by chlorosulfonic acid)." The freezing curve for this sample is shown as Curve III in Figure 3.

Figure 4 shows the infra-red absorption spectra of the isolated nonane. The curves illustrated were obtained by U. Liddel, of the Fixed Nitrogen Laboratory, United States Department of Agriculture.

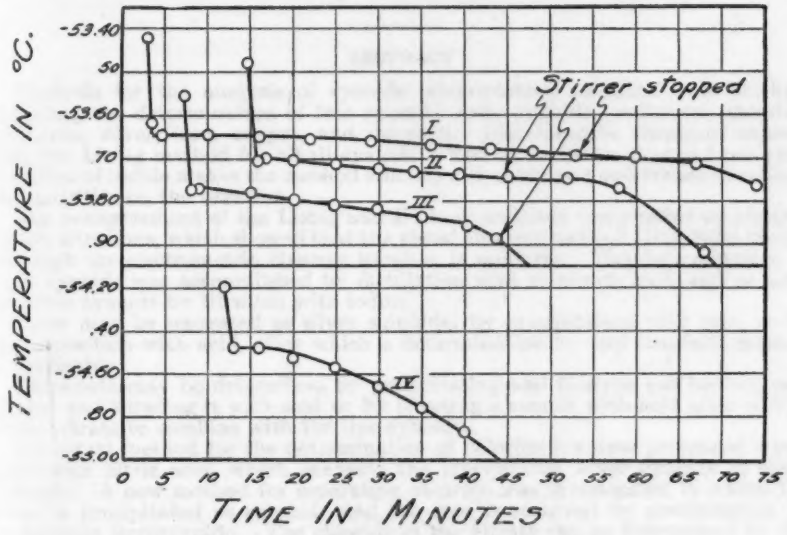

FIGURE 3.—*Freezing curves of n-nonane*

Curve I, best sample (by physical means).
II, synthetic n-nonane (Mair).
III, best sample (by chlorosulphonic acid).
IV, Lot II, main stock.

V. CONTENT OF *n*-NONANE IN THE CRUDE OIL

When allowance is made for losses which occurred in the various stages of the work, it is estimated that the crude petroleum used in this investigation contains about 1 per cent of *n*-nonane by weight.

VI. ACKNOWLEDGMENT

The writers are indebted to E. W. Washburn, chief of the chemistry division, Bureau of Standards, and director of this project, for his able advice throughout this investigation. Thanks are also expressed to R. T. Leslie for his many helpful suggestions in carrying out the present work.

WASHINGTON, August 17, 1931.

THE ANALYSIS OF CYANIDE SILVER-PLATING SOLUTIONS

By R. M. Wick

ABSTRACT

Methods for the analysis of cyanide silver-plating solutions were studied, including the determination of free cyanide, total cyanide, carbonate, chloride, ammonia, silver, iron, copper, and mercury. Electrometric titrations showed that the Liebig method for alkali cyanide is correct to better than 0.2 per cent. Addition of iodide makes the method still more accurate and overcomes the effects of impurities on the titration.

The nonagreement of the Liebig and Hannay methods was studied by electrometric titrations, which showed that the visual Hannay method gives high results although the electrometric Hannay titration is accurate. The determination of total cyanide was accomplished by distillation with sulphuric acid, and of total effective cyanide by titration with iodine.

Silver may be separated as silver sulphide, by precipitation with zinc, or by decomposition with acid, after which a determination by any standard method is applicable.

Carbonate may be determined by precipitating and filtering out barium carbonate and titrating it with acid or by titrating a sample with acid after adding silver nitrate to combine with the free cyanide.

The usual method for the determination of chloride involves prolonged treatment with nitric acid, which converts the precipitated silver cyanide to silver chloride. A new method for separating chloride was investigated in which the silver is precipitated as sulphide and the iron is removed by precipitation as manganous ferrocyanide. The chloride in the filtrate can be determined by the usual methods.

Iron and copper can be determined by the regular analytical methods after decomposition of the plating solution with sulphuric acid. Mercury can be determined by precipitation as sulphide along with silver sulphide. The mercuric sulphide is extracted from the mixed sulphide precipitate with sodium hydroxide, reprecipitated, and weighed.

A new method was developed for the determination of ammonia in cyanide solutions, in which the free cyanide is converted to the silver complex preparatory to the usual distillation. Direct distillation is not satisfactory because ammonia is formed by decomposition of alkali cyanide at elevated temperatures.

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I. INTRODUCTION

Much of the recent progress in the electroplating industry is due to the more general use of chemical analysis for the control of the solutions. High accuracy is usually not required, but it is important to know whether the methods that have been proposed or used yield results of the desired reliability in the presence of all the probable constituents, including impurities. In research work a higher degree of accuracy is sometimes needed. In the following study of silver-plating solutions both of these requirements have been considered, in the effort to develop control methods that are correct to at least 2 per cent and research methods accurate to 0.2 per cent.

As the methods for the determination of cyanide are most important in silver-plating baths and as they have been questioned in the literature, they were given special consideration, and their accuracy was determined by comparison with electrometric methods. In general, volumetric methods were investigated, as they are more convenient for control purposes.

II. COMPOSITION OF SILVER-PLATING SOLUTIONS

All commercial silver plating is done in cyanide solutions, from which relatively dense fine-grained deposits are secured, in contrast with the coarse deposits obtained from silver nitrate solutions, which are used for silver refining. Modern plating baths are prepared by dissolving silver cyanide in either potassium or sodium cyanide, the former being more commonly used. All methods of analysis, and hence the following discussions, apply equally to the potassium or sodium salts.

The principal constituent of the baths is potassium argentocyanide, $KAg(CN)_2$. The baths contain an excess of the alkali cyanide, which is known as the "free cyanide." Commercial solutions are about 0.25 *N* with respect to both silver and free cyanide. In addition they invariably contain alkali carbonate, which is sometimes added in the preparation of a new bath. In any case it forms in the solution by decomposition of the cyanide, and may accumulate to high concentrations. During the decomposition of cyanides, ammonia is usually formed, and hence is present in all used cyanide solutions. Its concentration is not likely to be high, as at the high pH of these solutions the ammonia is free and rapidly volatilizes, especially at elevated temperatures.

In former years the baths were made from silver chloride, and hence contained much alkali chloride. Some chloride is present in all commercial baths as a result of impurities in the chemicals or the water used. The baths are likely to contain iron, present as ferrocyanide. This enters from corrosion of the steel tanks, pipes, or hangers, especially if much chloride is present. Small amounts of copper may be introduced from the preceding "strike" solutions, to which copper is added, or from corrosion of the copper tank bars. Mercury may be introduced, especially into the strike solution, if mercury dips are used prior to silver plating. As mercury dips are now seldom used, such contamination is improbable.

For control the most common determinations are those for free cyanide and silver. Carbonate is occasionally determined, though the bath is not sensitive to small changes in the carbonate concentration. In this investigation the analytical methods for these three substances were examined, and the effects of other constituents upon the results were determined. Methods for estimating impurities were also studied.

Prior to the regular silver plating it is customary to apply flash coats of silver from "strike solutions." These generally have a high content of free cyanide and a low content of silver. In some cases copper is added to the strikes. In general the same methods of analysis are applied to the strikes as to the regular solutions, although the composition of the strikes is less critical.

III. ANALYTICAL METHODS

1. CYANIDE

A. ALKALI CYANIDE

As it is sometimes desirable to analyze the alkali cyanide used in the preparation of silver baths and as the free cyanide determination involves the titration of alkali cyanide, the methods for this determination were first investigated.

(1) TITRATION OF PURE SOLUTIONS.—(*a*) *Liebig method.*—Titration with silver nitrate, usually attributed to Liebig (1),[1] is most commonly used, either in its original form or with the addition of iodide. The accuracy of the Liebig method was questioned by Frary and Porter (2) because it gave lower results than the Hannay (mercuric chloride) titration. Thompson (3) prepared very pure potassium cyanide and with it showed that the Hannay method gives high results, and that

[1] Numbers in the text refer to the bibliography at the end of the paper.

the Liebig method is more accurate. Additional confirmation of the latter method was obtained in this investigation.

In the Liebig method (1) silver nitrate is added to a solution of alkali cyanide until reaction 1,

$$2\ KCN + AgNO_3 = KAg(CN)_2 + KNO_3 \quad (1)$$

is complete. On further addition of silver nitrate, reaction 2,

$$KAg(CN)_2 + AgNO_3 = 2\ AgCN + KNO_3 \quad (2)$$

begins, and results in the formation of insoluble silver cyanide. The appearance of the latter as an opalescence serves as the end point of reaction 1.

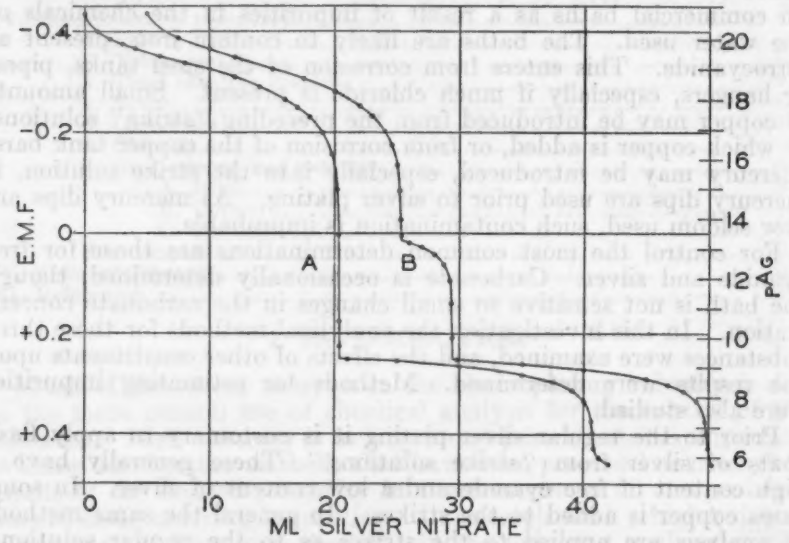

FIGURE 1.—*Electrometric titration of potassium cyanide with 0.1 N silver nitrate*

A, Without potassium iodide.
B, With potassium iodide.

(The origin of curve B is displaced 5 ml to the right of A.)

When potassium iodide is present in the titrated solution, reaction 3,

$$KI + AgNO_3 = AgI + KNO_3 \quad (3)$$

takes precedence over reaction 2 because the solubility of silver iodide is lower than that of silver cyanide. The appearance of silver iodide is then taken as the end point of reaction 1.

(*b*) *Electrometric method.*—As the above reactions involve the formation or removal of silver ions, their course may be followed electrometrically by using a silver electrode. The theory of the electrometric titration is discussed by Kolthoff and Furman (4). The application of the silver electrode to cyanide solutions was reported by W. D. Treadwell (5) and later by Müller and Lauterbach (6).

Curve A of Figure 1 shows the course of a typical titration made in this investigation, in which the potential of the silver electrode (E_h)

(or the corresponding pAg)[2] is plotted against the volume of 0.1 *N* silver nitrate added to 20 ml of approximately 0.2 *M* sodium cyanide. In this curve the first inflection marks the end of reaction 1 and the second the end of reaction 2. These two points of inflection were defined more closely by completing the titration with 0.01 *N* silver nitrate when they were approached. The results are shown in Figure 2, *A* and *B*, in which the points of inflection are defined by plotting $\frac{\Delta E}{\Delta V}$, that is, the rate of change of potential with the volume of reagent against the volume. It is evident that the second point of inflection is less sharp than the first, but both are readily defined.

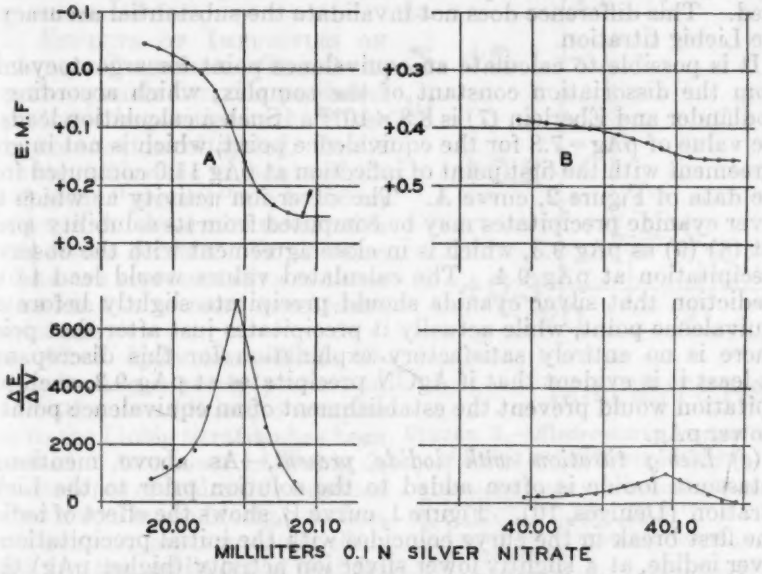

FIGURE 2.—*Points of inflection in electrometric titration of potassium cyanide without iodide, using 0.01 N silver nitrate near the end points*

A, First inflection.
B, Second inflection.

TABLE 1.—*Ratio of end points in electrometric titration of alkali cyanide*

Experiment No.	Volume of 0.1 *N* $AgNO_3$		Ratio
	First	Second	
	ml	*ml*	
9	20.35	40.70	2.000
41	20.05	40.05	1.998
48	19.85	39.70	2.000
59	20.40	40.84	2.002
Average			2.000

If these two points represent accurately the end points of reactions 1 and 2, the volume of silver nitrate required for the second point

[2] pAg, the negative logarithm of the silver ion activity, is analogous to pH.

should be twice that for the first. In Table 1 are shown the results of several electrometric titrations made from time to time. The close agreement of this ratio with the theoretical value is strong evidence that the reactions proceed exactly according to the equations. A previous publication (6) reported a deviation of 0.5 per cent in this ratio, but in this case only 10 ml of silver nitrate was used, and accordingly the precision was probably not much greater than the reported discrepancy.

As shown in Figure 2 A, the visual precipitation (marked by an arrow) of silver cyanide does not exactly coincide with the first point of inflection, though the discrepancy is only about 0.04 ml of 0.1 *N* $AgNO_3$, equivalent to 1 part in 500 if 20 ml of titrating solution be used. This difference does not invalidate the substantial accuracy of the Liebig titration.

It is possible to calculate an equivalence point for argentocyanide from the dissociation constant of the complex, which according to Bodländer and Eberlein (7) is 8.8×10^{-22}. Such a calculation leads to the value of pAg = 7.8 for the equivalence point, which is not in good agreement with the first point of inflection at pAg 11.0 computed from the data of Figure 2, curve A. The silver ion activity at which the silver cyanide precipitates may be computed from its solubility product (8) (9) as pAg 9.3, which is in close agreement with the observed precipitation at pAg 9.4. The calculated values would lead to the prediction that silver cyanide should precipitate slightly before the equivalence point, while actually it precipitates just after that point. There is no entirely satisfactory explanation for this discrepancy. At least it is evident that if AgCN precipitates at pAg 9.3, such precipitation would prevent the establishment of an equivalence point at a lower pAg.

(*c*) *Liebig titration with iodide present.*—As above mentioned, potassium iodide is often added to the solution prior to the Liebig titration (Denigès, 10). Figure 1, curve B, shows the effect of iodide. The first break in the curve coincides with the initial precipitation of silver iodide, at a slightly lower silver ion activity (higher pAg) than that at which silver cyanide precipitates, the second break in curve B, and at a point which approaches very closely to the measured equivalence point. It is evident, therefore, that the titration with iodide yields a more accurate result than the visual Liebig method. In pure solutions the difference is negligible, but, as will be shown, the iodide is especially effective in titrating contaminated solutions.

(*d*) *Comparison of Liebig and Hannay methods.*—A comparison between the Liebig and Hannay methods was made electrometrically. For the latter method the potential of a mercury electrode was measured during the addition of mercuric chloride to the solution, which contained a small amount of ammonia. In this titration the first reaction is

$$4KCN + HgCl_2 = K_2Hg(CN)_4 + 2KCl \qquad (4)$$

At the end point any excess of mercuric chloride reacts with the ammonia to form a white precipitate

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O \qquad (5)$$

In Figure 3 is shown the relation between the Hannay (*A*) and Liebig (*B*) titrations near the end points. The volumes of the

respective reagents consumed at the inflection points agree within 0.2 per cent with the equivalence, represented by the line *E*. However, the precipitation of silver cyanide occurs at the point *C*, which coincides closely with *E*, while that of the mercury compound occurs at *D*, which is several per cent beyond *E*. These results show clearly that reaction (4) of the Hannay method is quantitative, but that the visual end point, as defined by reaction (5), is seriously in error. The observed discrepancy between the two methods with visual end points is thus fully accounted for.

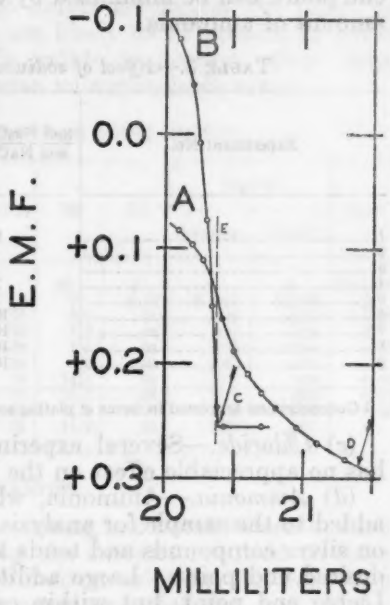

FIGURE 3.—*Electrometric comparison of Liebig and Hannay titrations*

A, Hannay titration with mercuric chloride.
B, Liebig titration with silver nitrate.
C, Precipitation of silver cyanide.
D, Precipitation of mercury compound.
E, Equivalence point.

(2) EFFECTS OF IMPURITIES ON THE LIEBIG TITRATION.—The effects upon the cyanide titration produced by probable impurities in the silver baths were next investigated. In the following tables the amounts of alkali cyanide "present" are based on electrometric determinations with no impurities present. In all cases the data are representative of those obtained in two or more concordant experiments.

(*a*) *Alkali hydroxide.*—While alkali hydroxide is rarely present in silver baths, its addition to samples prior to the Liebig titration has been suggested. As shown in Table 2, large amounts of hydroxide produce marked errors in the Liebig titration, which, however, are completely eliminated by the addition of iodide. These results confirm the statements of Clennell (11) and Sharwood (12).

TABLE 2.—*Effect of NaOH on Liebig titration*

Experiment No.	$\frac{\text{mol NaOH}}{\text{mol NaCN}}$	KI	NaCN		Error
			Present [1]	Found	
		g	*g*	*g*	*Per cent*
1	0	----------	0.1976	0.1980	+0.20
2	10	----------	.1974	.2074	+5.06
3	10	----------	.1976	.2075	+5.01
4	10	0.04	.1976	.1978	+.10
5	10	.04	.1975	.1977	+.10

[1] Based on electrometric end point with no additions.

(*b*) *Alkali carbonate.*—Table 3 shows that high concentrations of carbonate, probably greater than are present in a silver bath, produce an error in the Liebig titration of less than 1 per cent. (The carbonate has no effect on the electrometric end point.) The effect of

carbonate is completely overcome by the use of iodide, as previously noted by Clennell (11), Sharwood (12), and Sanigar (13). As shown by the last author, the tendency of carbonate to cause the formation of a difficultly soluble granular precipitate which obscures the true end point, can be minimized by dilution, or by the addition of a small amount of ammonia.

TABLE 3.—*Effect of sodium carbonate on the Liebig titration*

Experiment No.	$\frac{\text{mol } Na_2CO_3}{\text{mol NaCN}}$	Na_2CO_3	KI	NaCN		Error
				Present	Found	
		g/l[1]	g	g	g	Per cent
1	0			0.2005	0.2009	+0.20
2	.1	2.65		.2006	.2010	+.20
3	.1	2.65		.1995	.1999	+.20
4	1	26.5		.1991	.1998	+.35
5	1	26.5		.1976	.1984	+.40
6	10	26.5		.1990	.2006	+.80
7	10	26.5		.1995	.2010	+.75
8	10	26.5	0.04	.1996	.1996	0
9	10	26.5	.04	.2001	.2000	−.05

[1] Concentration expressed in terms of plating solution.

(*c*) *Chloride.*—Several experiments indicated that alkali chloride has no appreciable effect on the Liebig titration.

(*d*) *Ammonia.*—Ammonia, which may be present in the bath or added to the sample for analysis (10), (11), (12), has a solvent action on silver compounds and tends to maintain a clear solution up to the desired end point. Large additions cause gross errors in the visual Liebig end point, but within certain limits the presence of iodide eliminates this effect of ammonia. However, according to Treadwell (5), a large excess of ammonia dissolves silver iodide and yields high results. These observations are all confirmed in Table 4. The fact that the silver electrode potential at equivalence is more negative in the presence of ammonia, indicates that the latter has reacted with the argentocyanide to form a still less dissociated compound. When the ammonia is more than equivalent to the cyanide, the second electrometric end point vanishes.

TABLE 4.—*Effect of ammonium hydroxide on the Liebig titration*

Experiment No.	$\frac{\text{mol } NH_4OH}{\text{mol NaCN}}$	NH_4OH	KI	NaCN					
				Present	Found				
					Electrometric			Liebig	
					Equivalence potential E_h		Error		Error
		g/l[1]	g	g		g	Per cent	g	Per cent
1	0			0.1977	+0.161	0.1977	0	0.1981	+0.2
2	0.1	0.9		.1976	+.106	.1970	−0.3	.1984	+.35
3	1	8.8		.1971	+.034	.1963	−.4	.2037	+3.5
4	10	87.6		.1975	−.034	.1961	−.7	.2705	+37.0
5	1	8.8	0.04	.1951		.1951		.1956	+.3
6	10	87.6	.04	.1999		.1998		.2006	+.3

[1] In terms of plating solution.

(*e*) *Ferrocyanide.*—It has been reported (5), (11), (12), that ferrocyanides cause high results in the Liebig titration and that iodide prevents this error. The ferrocyanide also fosters the formation of a curdy precipitate that redissolves slowly. The results in Table 5 show that the presence of sufficient iodide eliminates the effect of ferrocyanide in concentrations that are likely to be present in silver plating baths. Unless considerable iodide is present, very large amounts of the ferrocyanide still cause an appreciable error.

TABLE 5.—*Effect of ferrocyanide on Liebig titration*

Experiment No.	$Na_4Fe(CN)_6$	Fe	KI	NaCN		Error
				Present	Found	
	g/l [1]	g/l [1]	g	g	g	Per cent
1	0	0	0.04	0.2186	0.2186	0
2	20	3.7	.04	.1948	.1953	+0.25
3	20	3.7	.04	.1875	.1875	0
4	38	7.0	.04	.2134	.2140	+.27
5	38	7.0	.04	.1852	.1857	+.27
6	78	14.5	.04	.1978	.1986	+.40
7	78	14.5	.04	.1875	.1885	+.53
8	76	14.0	.25	.1985	.1986	+.05
9	61	11.2	.25	.2487	.2487	0

[1] In terms of plating solution.

B. FREE CYANIDE

The term "free cyanide" in electroplating has usually been defined as the excess of alkali cyanide above the amount required to form some complex, such as $KAg(CN)_2$. For silver solutions this definition is satisfactory, because (*a*) the silver complex is definite, and (*b*) the titration with silver nitrate in the presence of iodide yields results that correspond closely to this compound.

As above noted, the silver plating solutions contain only one stable complex, $KAg(CN)_2$, which is also formed during the titration of alkali cyanide with silver nitrate. The only essential difference therefore between a silver solution containing free cyanide and a partly titrated solution of alkali cyanide, is that the latter contains a quantity of alkali nitrate equivalent to the silver nitrate added. Numerous observations here and elsewhere have shown that such an amount of nitrate has no measurable effect on the titration. Sanigar (13) found that the addition of over 7 g of potassium nitrate produced an error of only 1 part in 400 in the Liebig titration of 10 ml of 0.5 *M* KCN. As this content of nitrate was about 300 times that formed in the titration, it is evident that the latter amount can have no significant effect.

It is obvious, therefore, that all the data obtained in the titration of alkali cyanide apply directly to the determination of free cyanide in silver-plating solutions, and that by the addition of iodide the effects of all probable impurities upon the titration can be effectively eliminated.

C. TOTAL CYANIDE

Most of the heavy-metal impurities in a silver bath exist as double cyanides, such as $K_2Cu(CN)_3$, $K_2Hg(CN)_4$, and $K_4Fe(CN)_6$. The "total cyanide" includes that present in all such compounds plus that in $KAg(CN)_2$ and the free KCN. For pure silver solutions it is possible to compute the content of total cyanide, which is the sum of

the free cyanide and that combined with the determined content of silver. For contaminated solutions such calculations are of doubtful value because of possible errors in the determination of all the metals present, and of uncertainty as to the composition of the corresponding complex cyanides.

For many cyanide solutions, including those of silver, distillation with sulphuric acid followed by absorption and titration of the evolved hydrocyanic acid, yields fairly reliable results for total cyanide. In silver plating the determination of total cyanide is of interest chiefly for research purposes. The distillation method is applicable to other cyanide plating baths, and may be of value in the control of zinc or brass baths, in which the free cyanide is less readily determined.

Distillation is carried out after the addition of about 250 ml of water and 10 ml of 1:1 sulphuric acid, and continued until the precipitate formed on acidification has dissolved and at least half of the solution has distilled over. When chloride is present in the plating solution a residue of insoluble silver chloride persists which makes difficult the detection of complete decomposition, but does not otherwise cause error. Complete recovery of cyanide from ferrocyanide is not possible by acid treatment unless other metals are present which form readily decomposible ferrocyanides. Additions of copper as cuprous chloride was suggested by H. E. Williams (14) as the basis of a method for estimating ferrocyanides. In the present investigation it was found that equally good results are obtainable when complex silver cyanide is present, so that addition of a cuprous salt to the sample is not essential. When alone, cuprous cyanide requires the presence of a chloride (or hydrochloric acid) to complete its decomposition, but in the presence of ferrocyanide no chloride is needed. In silver-plating solutions it is not necessary to add a chloride to decompose any copper cyanide that may be present, as the commercial solutions invariably contain some ferrocyanide.

TABLE 6.—*Determination of total cyanide by distillation and titration*

Experiment No.	Constituents of sample	Cyanides (CN)		
		Present	Found	Error
		g	*g*	*Per cent*
1	$NaCN$	0.1148	0.1145	−0.26
2	do	.1112	.1109	−.27
3	$NaAg(CN)_2$	.1999	.1988	−.55
4	do	.2006	.1994	−.60
5	$Na_4Fe(CN)_6$	.2062	.2022	−1.94
6	do	.2081	.2039	−2.02
7	do	.2084	.2046	−1.82
8	$CuCN$	.2089	.2065	−1.15
9	do	.2081	.2057	−1.15
10	$NaCN$ (0.4 *M*), $NaAg(CN)_2$ (0.2 *M*), $Na_4Fe(CN)_6$ (0.05 *M*)	.3006	.2988	−.60
11	do	.2251	.2242	−.40

Typical results obtained by this method are given in Table 6. For $NaCN$ and $NaAg(CN)_2$, the major bath constituents, good recovery of cyanide is obtained The results of separate determinations of the minor constituents, such as $Na_4Fe(CN)_6$ and $CuCN$, were slightly low. Since these substances normally represent only a small fraction of the total cyanide present in a silver bath, this error is not

serious. The data for a synthetic plating solution show that 99.5 per cent of the total cyanide was recovered.

D. TOTAL EFFECTIVE CYANIDE

Among the constituents of the silver-plating bath the ferrocyanide is the most stable on electrolysis, and it is at least doubtful whether it has any marked effects upon the operation of the baths or the character of the deposits. For certain purposes it may therefore be desirable to determine what may be designated as the "total effective cyanide"; that is, the total content of the CN radical exclusive of that present as ferrocyanide.

Titration with iodine was found satisfactory for the total effective cyanide in silver baths. This method is similar to that used by H. Baines (15) for the determination of silver halides after they are dissolved in alkali cyanide. Iodine reacts with alkali cyanide according to equation 6.

$$KCN + I_2 = KI + CNI \qquad (6)$$

If silver is also present, reaction 7 follows.

$$KAg(CN)_2 + 2I_2 = KI + AgI + 2CNI \qquad (7)$$

When a silver solution containing free cyanide is titrated, the appearance of a precipitate of AgI serves as the endpoint of reaction 6, and measures the free cyanide. The initial precipitation of silver iodide is more readily detected and more reliable in a relatively concentrated solution containing an added salt such as sodium chloride. The iodo-starch reaction may be used to show the endpoint of reaction 7, provided the dilution is sufficient to prevent interference by the reddish color of cyanogen iodide. The total concentration of cyanide should be not more than about 0.002 *M* for the second titration, therefore the sample should be greatly diluted prior to the final end point.

When copper is present, it reacts approximately according to equation 8:

$$K_2Cu(CN)_3 + 3I_2 = 2KaI + CuI + 3CNI \qquad (8)$$

The mercury complex is similarly decomposed:

$$K_2Hg(CN)_4 + 4I_2 = 2KI + HgI_2 + 4CNI \qquad (9)$$

The exact composition of these complexes is in doubt, and these reactions may not be correct. Ferrocyanide is only slowly oxidized by iodine, and as will be shown, it has little effect unless its concentration is high.

The iodine solution is unstable and must be frequently restandardized. This may be done against a standard alkali cyanide solution, or preferably a standard silver cyanide solution containing free cyanide. In the latter solution, the content of silver is more nearly constant than that of alkali cyanide. Hence by using such a solution and basing the standardization on the second step in the titration, reliable results are obtained.

TABLE 7.—*Effects of impurities on the determination of total effective cyanide with iodine. Solution 0.25 N in silver and 0.25 M in free cyanide*

Experiment No.	Impurities				Total effective cyanide		Error
	Equivalent to concentration in plating solution				Present millimols	Found millimols	
	Na_2CO_3	Fe	Cu	Hg			
	g/l	*g/l*	*g/l*	*g/l*			*Per cent*
1	125				2.000	2.000	0
2	250				2.000	2.006	+.3
3	500				2.000	2.006	+.3
4		3.8			2.000	2.004	+.2
5		7.5			2.000	2.008	+.4
6		15.1			2.000	2.028	+1.4
7			1.7		2.084	2.093	+.4
8			3.0		1.993	2.025	+1.6
9			4.4		1.903	1.944	+2.1
10				1.8	1.658	1.658	0
11				3.6	1.658	1.656	−.1
12				7.2	1.658	1.654	−.2

In Table 7 are shown the results obtained by titrating with iodine a known amount of alkali cyanide to which was added a definite amount of silver nitrate and the designated amounts of the specified impurities. The amounts of cyanide introduced with the copper and mercury were included in that "present," but not the cyanide contained in the ferrocyanide. The results show that large amounts of carbonate have no effect. Relatively high concentrations of iron or copper produce appreciable errors. Small amounts of mercury have no marked effect, but very large amounts of mercury or copper entirely obscure the end point. The method therefore does not possess high accuracy in excessively contaminated solutions.

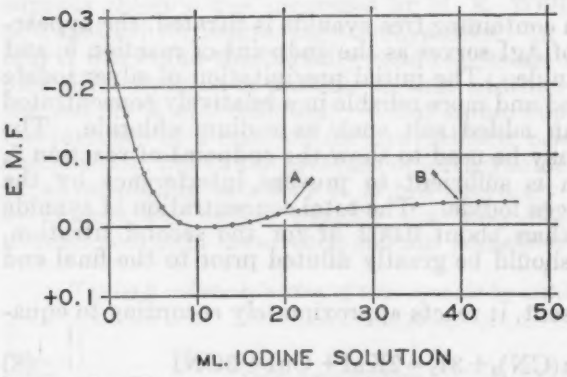

FIGURE 4.—*Electrometric titration of silver cyanide solution with iodine*

A, Initial precipitation of silver iodide, the end point for the titration of free cyanide.
B, Iodo-starch reaction, the end point for titration of total cyanide.

The iodine titration of cyanide was also followed electrometrically with a silver electrode, with the results shown in Figure 4. The solution contained two equivalents of free cyanide for one of silver. The visible end points of the two reactions occurred at the points *A* and *B*, at which the inflections are not sufficiently sharp to accurately define the reactions. In the first portion of the curve the silver ion activity reached a maximum when about half the free cyanide was titrated. This behavior probably represents the formation of some complex between the argentocyanide ion and iodine.

2. SILVER

A. SEPARATION FROM THE CYANIDE

Most methods for the determination of silver (except the electrolytic method) necessitate the separation of the silver from the cyanide. This can be accomplished either by precipitation of the silver or by decomposition of the cyanide solution.

(1) PRECIPITATION OF SILVER.—(*a*) *As sulphide.*—Silver can be precipitated by the addition of ammonium sulphide to the cyanide solution. This procedure separates it not only from the cyanide, but also from ferrocyanide and metallic impurities, excepting mercury which also precipitates as sulphide. This method is described by Brook and Holmes (16), who ascribe it to Wright (17). Coagulation and complete precipitation of the silver sulphide are favored by boiling the ammoniacal solution. In this boiling, ammonium cyanide is volatilized (18). The silver sulphide can then be filtered out, washed, and dissolved in nitric acid to prepare it for titration.

(*b*) *As silver.*—Metallic silver can be precipitated by boiling the solution with pure granulated zinc, Clevenger (19). The precipitate, which contains the silver and excess of zinc, is then dissolved in nitric acid.

(2) DECOMPOSITION OF THE CYANIDE.—When sulphuric acid is added to the cyanide solution silver cyanide is precipitated and hydrocyanic acid is evolved. The operation should therefore be conducted with very good ventilation. On evaporation the silver cyanide slowly dissolves. This dissolution can be hastened by adding initially a volume of concentrated sulphuric acid equal to twice the volume of plating solution. When commercial cyanide solutions are evaporated to fumes with sulphuric acid, darkening usually occurs. This disappears on the addition of a few milliliters of concentrated nitric acid and reevaporation to fumes. After cooling, the residue is dissolved in water. The resulting solution contains sulphates of all the metals present in the original bath.

B. DETERMINATION OF SILVER

(1) VOLHARD TITRATION.—The details of this well-known method (20) are discussed by Hillebrand and Lundell (21). The solution of silver nitrate or silver sulphate obtained by any of the above procedures is titrated with thiocyanate solution, using ferric alum as the indicator. The thiocyanate is standardized against silver nitrate. The presence of filter paper remaining from the solution of the silver or silver sulphide precipitate is unobjectionable. Usually it is preferable for high accuracy to treat the silver nitrate sample used for standardization in the same way as the plating solution. If small amounts of mercury are present, they will be included in this titration.

(2) PRECIPITATION AS SILVER CHLORIDE.—Silver chloride can be precipitated by the addition of hydrochloric acid to the silver solution obtained by any of the above methods. It can then be weighed or dissolved in standard cyanide and the excess cyanide determined by the Liebig titration, preferably with iodide present. It can also be determined after solution in cyanide, by titration with iodine (15) as described above. In the latter procedure it is not necessary to standardize the alkali cyanide, as the silver is equivalent to the combined cyanide as determined in the second part of the titration.

(3) ELECTROLYTIC DETERMINATION.—Silver can be directly deposited from a diluted sample of the plating solution, to which additional cyanide has been added.

C. COMPARISON OF METHODS

In Table 8 are shown the results obtained by some of the above procedures upon a synthetic plating solution containing the usual impurities. These results show that all of the methods are sufficiently accurate for control, though the electrolytic method gives slightly low results. The choice of procedure is therefore largely one of expediency. The Volhard titration is almost invariably used in the industry. Decomposition with acid is preferable to the sulphide precipitation because no filtration is required.

TABLE 8.—*Determination of silver in synthetic contaminated silver-plating solutions*

Experiment No.	Separation	Determination	Silver		
			Present	Found	Error
			g	*g*	*Per cent*
1	Silver sulphide	Volhard	0.5016	0.5026	+0.20
2	do	do	.5016	.4999	−.34
3	do	do	.5016	.5023	+.14
4	By zinc	do	.3010	.3011	+.03
5	do	do	.3210	.3213	+.10
6	do	do	.3411	.3407	−.12
7	Acid evaporation	do	.5016	.5016	0
8	do	do	.5016	.5016	0
9	do	do	.5016	.5015	−.02
10		Electrolytic	.4963	.4941	−.44
11			.4961	.4932	−.58

3. CARBONATE

A. BARIUM CARBONATE METHOD

The usual method for determining carbonate in cyanide solutions is to precipitate and filter out barium carbonate and titrate it with acid, with methyl orange as indicator. Brook and Holmes (16) recommend barium cyanide as the precipitant, but experiments have shown that barium chloride or nitrate is equally satisfactory. As the alkaline solutions readily absorb carbon dioxide, the precipitation and filtration should be done as rapidly as possible. Operation in a CO_2-free atmosphere is unnecessary except for very high accuracy. As shown in Table 9, the presence of ferrocyanide causes no significant error.

TABLE 9.—*Determination of carbonate in synthetic contaminated silver-plating solutions*

Experiment No.	Method	Iron	$NaCO_3$		
			Present	Found	Error
		g/l	*g*	*g*	*Per cent*
1	$BaCO_3$		0.4710	0.4714	+0.09
2	do		.4669	.4685	+.34
3	do	0.8	.4740	.4754	+.30
4	Direct titration		.9320	.9340	+.21
5	do		.9198	.9242	+.48
6	do	.8	.9269	.9231	−.41
7	do	.8	.9159	.9146	−.14

B. TITRATION AFTER ADDITION OF SILVER NITRATE

Silver-plating solutions have a pH of about 11, caused by the hydrolysis of the free cyanide as well as of carbonate. If silver nitrate is added to a solution containing no carbonate until the free cyanide is removed (Liebig titration) the resulting argentocyanide has a pH of about 7. Therefore any residual alkalinity in a plating solution similarly treated is due to carbonate (or less commonly to free alkali). As shown by Clennell (22), it is therefore possible to titrate the carbonate with acid, after completing the Liebig titration (conducted with or without iodide). Phenolphthalein is used as the indicator, to avoid reducing the pH below 7, where the argentocyanide would decompose. The titration therefore represents the conversion of carbonate to bicarbonate. F. Muhlert (23) modified the Clennell method by adding sufficient silver nitrate to precipitate all the cyanide, filtering out the silver cyanide, and titrating the carbonate. This method has no obvious advantages.

As shown in Table 9, the direct titration yields satisfactory results, even on contaminated solutions. As it is simpler and more rapid than the barium carbonate precipitation, it is preferable for control purposes.

4. CHLORIDE

The determination of chloride in alkali cyanide solutions is reviewed by Polstorff and Meyer (24). The method of W. Borchers (25) depends upon the decomposition of silver cyanide by concentrated nitric acid and the formation of insoluble silver chloride. When nitric acid is added to a silver-plating solution, a mixture of silver cyanide and chloride is first precipitated. When the solution is boiled the silver cyanide slowly dissolves and leaves a precipitate of silver chloride. In order that this shall include all the chloride present in the bath the silver must be in excess. This is usually the case, but for a solution that is high in chlorides it is advisable to add silver nitrate. The silver chloride can then be weighed or titrated by methods described above. As shown in Table 10 the results by this method are usually about 1 per cent low for contaminated solutions. This indicates that under the conditions used a small amount of the silver chloride is decomposed by the boiling nitric acid.

TABLE 10.—*Determination of chloride in synthetic contaminated silver-plating solutions (containing 27 g/l Na_2CO_3 and 52 g/l $Na_4Fe(CN)_6$*

Method of separation	Determination	Sodium chloride		
		Present	Found	Error
		g	*g*	*Per cent*
Borchers	Gravimetric	0.2414	0.2376	−1.6
Do	do	.2439	.2321	−1.2
Do	do	.2398	.2367	−1.3
Alternate	$AgNO_3$+NaCNS	.3664	.3748	+2.3
Do	do	.3664	.3730	+1.8
Do	do	.3664	.3727	+1.7

A new procedure for separating the chloride from the other constituents of the bath was investigated. In brief, the method involves (*a*) removal of silver as sulphide, (*b*) decomposition of the cyanide

by boiling the ammoniacal solution, and (*c*) precipitation of the ferrocyanide by the addition of a manganous salt. Qualitative tests showed that manganous ferrocyanide can be filtered and washed satisfactorily, while most of the other insoluble ferrocyanides are colloidal. The addition of manganous sulphate removes carbonate as well as ferrocyanide. The chloride may be determined in the resultant filtrate by numerous methods. Probably the most convenient of these is to acidify and titrate with silver nitrate, either directly with chromate indicator or by back titration of excess silver with thiocyanate.

Table 10 shows that the results are approximately correct though somewhat high for badly contaminated solutions. The method probably warrants further study.

5. IRON, COPPER, AND MERCURY

If the original plating solution is evaporated with sulphuric acid and the silver is removed as chloride, the filtrate contains the iron, copper, and mercury as sulphates. If silver is precipitated as sulphide the mercury accompanies it, and the filtrate which contains the iron and copper can then be decomposed with acid.

After the metals are obtained as sulphates, the usual methods of separation and determination can be applied. For example iron can be precipitated with ammonia and determined gravimetrically or volumetrically. The copper can be determined in the filtrate either volumetrically or electrolytically.

Mercury is best determined in the ammonium sulphide precipitate containing also the silver sulphide. The precipitate is treated with potassium hydroxide and ammonium sulphide, which mixture dissolves the mercuric sulphide. The silver sulphide is filtered out, and the mercuric sulphide is reprecipitated by boiling the filtrate with ammonium nitrate. The precipitate is filtered on a weighed Gooch crucible, washed successively with water, alcohol, carbon disulphide and ether, dried at 110° C. and weighed as HgS.

TABLE 11.—*Determination of iron, copper, and mercury in synthetic contaminated silver-plating solutions*

Experiment No.	Present			Found	Error
	Iron	Copper	Mercury		
	g	*g*	*g*	*g*	*Per cent*
1	0.6092			0.6085	−0.11
2	.6390			.6400	+.16
3		0.1575		.1578	+.19
4		.1667		.1665	−.12
5			0.0200	.0200	0
6			.0200	.0194	−3.0

Table 11 gives typical results obtained for these metals in synthetic silver solutions. For the small amount of mercury present the three per cent error reported in one determination was equivalent to only 0.6 mg of Hg. Evidently the methods described meet all the usual requirements for the determination of these impurities.

6. AMMONIA

Ammonia is formed in cyanide plating baths by the decomposition of alkali cyanide either through hydrolysis or oxidation, represented respectively by equations 10 and 11.

$$KCN + 2H_2O = HCOOK + NH_3 \quad (10)$$

$$2KCN + 2H_2O + 2KOH + O_2 = 2K_2CO_3 + 2NH_3 \quad (11)$$

No quantitative data are available concerning the extent to which ammonia exists in commercial plating baths, or the rôle which it plays in electrodeposition.

Clennell (11) refers to a method of Bettel (26) for determining ammonia in cyanide solutions, but does not comment on its accuracy. This method involves complete precipitation of cyanogen compounds with silver, filtration, and distillation of the solution after the addition of a few drops of acid. The method appears complicated and of doubtful accuracy. In the course of this work a simple and accurate method has been developed which may be applied to cyanide plating solutions.

In an attempt to determine ammonia by direct distillation it was found that reaction 10 proceeds so rapidly at the boiling temperature that an appreciable amount of ammonia is formed during the distillation. An effort was then made to carry the ammonia over in a stream of air, but at either 25° C. or 50° C. this procedure was found to give incomplete recovery.

Preliminary experiments showed that the argentocyanide complex formed when silver nitrate is added to alkali cyanide (equation 1) is stable on boiling. It therefore seemed possible to determine ammonia present in alkali cyanide solution by "fixing" the free cyanide with silver nitrate and, after the addition of alkali, distilling into standardized acid and titrating the excess of the acid.

TABLE 12.—*Determination of ammonia by distillation after addition of $AgNO_3$ and NaOH*

Experiment No.	NaCN	NH_3		Error
		Added	Found	
	g	*g*	*g*	*Per cent*
1	5.00	0	0.0017	
2		0	[1].0009	
3	1.85	0	.0004	
4		0	[1].0003	
5	1.85	.0472	[2].0469	−0.6
6	1.85	.0480	[2].0474	−1.2

[1] Second distillation of preceding solution after adding water.
[2] After deducting blank of 0.0004 g.

Table 12 shows that this method is satisfactory with moderate concentrations of cyanide. Blank distillations were first made on a 5 g and a 1.85 g sample of sodium cyanide, the latter amount being equivalent to 50 ml of a typical plating solution. The fact that a higher blank was obtained with 5 g of NaCN, and that in each case a small blank was obtained on a second distillation, indicates that there may be slight decomposition of the double cyanide, which is, however, negligible for the usual concentrations employed.

Part of the blank might be due to a trace of the solution being carried over as spray, although precautions to prevent this were used. Any significant error from this source would be indicated by the appearance of turbidity in the distillate, which would be cause for rejecting the determination.

The results for known small amounts of ammonia are very satisfactory. An old commercial silver-plating solution to which no ammonia had ever been added was analyzed by this method and found to contain 0.58 g NH_3 per liter, equivalent to 0.034 *N*. Further observations willl be required to determine whether this concentration is typical or significant. Pan (27) has recently advised the addition of ammonia to silver baths. The above method for determining ammonia is probably applicable to other cyanide plating solutions, such as those of copper and brass.

IV. RECOMMENDED PROCEDURES

The following explicit directions for the various determinations refer especially to the control of commercial plating solutions that may contain any of the usual impurities. To avoid confusion, only one method is described for each constituent. This selection is based on convenience and reliability as judged from the above experiments.

1. FREE CYANIDE

To a 20 ml sample of the plating solution add 0.1 g of potassium iodide (or 0.2 g for badly contaminated solutions). Dilute to 250 ml and titrate with 0.1 *N* silver-nitrate solution. The end point of the titration is the first appearance of opalescence, best observed with a black background.

1 ml 0.1 *N* $AgNO_3 \backsimeq$ 0.00980 g NaCN or 0.01302 g KCN

2. TOTAL CYANIDE

Dilute a fresh 10 ml sample of plating solution to 250 ml in a 500 ml distilling flask. Add through a dropping funnel 10 ml of 1:1 sulphuric acid and distill into 100 ml of 2 per cent sodium-hydroxide solution in a receiving flask. Boil the contents of the flask without bumping, until a clear solution results [3] and until half of the solution has distilled. Titrate the sodium cyanide in the receiving flask with 0.1 *N* silver-nitrate solution, using potassium iodide indicator, according to procedure 1.

3. TOTAL EFFECTIVE CYANIDE (EXCLUDING FERROCYANIDE)

Dilute 50 ml of the plating solution to 500 ml in a graduated flask. To a 25 ml aliquot (2.5 ml of the original) add 50 ml of a 10 per cent sodium-chloride solution containing 2 ml of concentrated ammonium hydroxide per liter, and titrate with 0.1 *N* iodine solution to the first visible turbidity. The volume of iodine consumed is proportional to the free cyanide.

Dilute the partially titrated sample to about 1 liter, add 5 ml of starch solution (0.5 per cent), and continue the titration with iodine

[3] If chloride is present, however, a permanent residue of AgCl will be observed.

until a faint but permanent blue color is formed. This second volume of iodine solution is proportional to the combined cyanide, and the sum is equivalent to the "total effective cyanide."

1 ml 0.1 *N* I_2 ⇔ 0.00245 g NaCN or 0.00326 g KCN

4. SILVER

Treat 10 ml of plating solution with 20 ml of concentrated sulphuric acid. Evaporate to fumes of sulphuric acid in a well-ventilated hood. Add a few drops of concentrated nitric acid if necessary to hasten decomposition of organic matter and reevaporate to fumes; cool, dilute to 150 ml, and warm until all solids are dissolved. Add 3 ml of saturated ferric ammonium alum solution and titrate with 0.1 *N* potassium thiocyanate to the appearance of a pink coloration.

1 ml 0.1 *N* KCNS ⇔ 0.01079 g Ag

5. CARBONATE

To the solution resulting from the Liebig titration for free cyanide (procedure 1) add a few drops of phenolphthalein solution and titrate with 0.5 *N* hydrochloric acid until the pink color is completely discharged.

1 ml 0.5 *N* HCl ⇔ 0.0530 g Na_2CO_3 or 0.0691 g K_2CO_3

6. CHLORIDE

To 10 ml of silver-plating solution add 20 ml of concentrated nitric acid under a hood. (If the solution is high in chloride, add an excess of silver nitrate before adding the acid.) Heat until decomposition is complete, as indicated by the precipitate becoming nearly white. Continue the digestion for one-half hour, keeping the volume constant by the addition of concentrated nitric acid. Dilute to 75 ml, make alkaline with concentrated ammonium hydroxide, and filter out the ferric hydroxide. Dissolve the ferric hydoxide in nitric acid and reprecipitate with ammonia; filter and combine the two filtrates. Acidify the combined filtrates with nitric acid, filter the silver chloride on a tared Gooch crucible, dry, and weigh as AgCl.

Factor AgCl→NaCl = 0.408

AgCl→KCl = 0.520

7. IRON, COPPER, AND MERCURY

A. IRON

Decompose a 10 ml sample of plating solution with 20 ml of concentrated sulphuric acid. Evaporate to fumes in a hood. If necessary, add a little concentrated nitric acid to destroy organic matter and reevaporate to fumes; cool, dilute to 150 ml, and warm to obtain complete solution of metal salts. Filter out any silica. Make the solution slightly alkaline with ammonium hydroxide, heat to coagulate the precipitate, and filter out the ferric hydroxide. (A blue filtrate indicates the presence of copper.) Dissolve the ferric hydroxide in hot 1:1 hydrochloric acid. Reprecipitate with ammonia, filter, and redissolve the ferric hydroxide.

Dilute the ferric-chloride solution to 50–75 ml, heat almost to boiling, and reduce the iron with stannous chloride,[4] added drop by drop, with only one or two drops in excess. Cool and add quickly 20 ml of a saturated mercuric-chloride solution and let stand three minutes. Add 15 ml of phosphoric-hydrochloric-acid mixture,[5] three drops diphenylamine indicator,[6] and titrate with 0.1 *N* bichromate solution. At the end point the solution changes from green to bluish green and finally to an intense violet blue with one drop of bichromate.

$$1 \text{ ml } 0.1\ N\ K_2Cr_2O_7 \backsimeq 0.00558 \text{ g Fe}$$

B. COPPER

A blue filtrate from the iron separation (7–A) indicates the presence of copper. To 10 ml of plating solution diluted to 100 ml add 3 ml of 6 *N* ammonium-sulphide solution. Heat almost to boiling, until the precipitate of silver sulphide has completely coagulated. Filter and evaporate the filtrate to about 10 ml. Cool and cautiously add 20 ml of concentrated sulphuric acid, evaporate to fumes, cool, dilute to 150 ml, and warm to obtain complete solution. Heat to 60°–70° C. and electrolyze, using a platinum or copper gauze cathode and a platinum anode. Weigh as Cu.

C. MERCURY

To a 20 ml sample of plating solution diluted to 100 ml add 5 ml of 6 *N* ammonium-sulphide solution. Heat the solution until the sulphides completely coagulate. Filter and wash. Treat the precipitate with 100 ml of 0.1 *N* sodium hydroxide and 1 ml of ammonium sulphide. Digest on a steam bath for one-half hour. Filter and wash. To the filtrate add 10 ml of 10 per cent ammonium-nitrate solution and warm; a black precipitate indicates the presence of mercury. Boil off the ammonia, filter on a tared Gooch crucible, wash with water, alcohol, carbon disulphide, and ether. Dry at 110° C. and weigh as HgS.

$$\text{Factor } HgS \rightarrow Hg = 0.862$$

8. AMMONIA

Titrate a fresh 50 ml sample of plating solution with 0.5 *N* silver nitrate, using potassium iodide according to procedure 1. Dilute to 250 ml in a 500 ml Kjeldahl flask, add 10 ml of 10 per cent sodium-hydroxide solution, and distill with a good trap into 50 ml of 0.1 *N* hydrochloric acid which has been diluted to 125 ml in the receiving flask. Boil the contents of the flask without bumping, until half of the solution has distilled. Titrate the residual acid in the receiving flask with 0.1 *N* sodium hydroxide, using methyl orange as indicator. The difference between the initial and final amounts of hydrochloric acid corresponds to the ammonia.

$$1 \text{ ml } 0.1\ N\ HCl \backsimeq 0.00170 \text{ g } NH_3$$

[4] 115 g $SnCl_2.2H_2O$ dissolved in 170 ml HCl (s. g. 1.18) diluted to 1 liter and stored in a bottle containing a piece of pure tin.
[5] 450 ml/l H_3PO_4 (s. g. 1.70) and 500 ml/l HCl (s. g. 1.18).
[6] 1 gram indicator in 100 ml H_2SO_4 (s. g. 1.84).

V. ACKNOWLEDGMENTS

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SILVERING AND EVACUATING PYREX DEWAR FLASKS

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ABSTRACT

A method of silvering and evacuating Pyrex Dewar flasks is described. The insulating properties of silvered flasks prepared in the way described in this paper are such that even in the wide-mouth cylindrical flasks filled with liquid air near to the lip there is no boiling, the change of the liquid air to the gaseous phase taking place entirely by surface evaporation. Details of the preparation of the surfaces to be silvered, the silvering process, baking out, and the sealing off procedure are included. The principal features of the process are: (1) some modification of the concentration of the reagents in the Brashear formula for silvering, (2) methods of preventing the silver coat from being spoiled when heating to a high temperature during evacuation, (3) baking out in two stages of decreasing temperature, (4) pumping off the gases evolved while sealing off before completing the seal.

The effect of high temperatures on the reflectivity of the vacuum side of a silvered glass surface was investigated. From measurements of the rate of evaporation of liquid air and liquid hydrogen in a sample flask, it was found that the residual gas between the walls was responsible for one-fourth the heat transferred across the vacuum space of the flask filled with liquid air. Calculations based on these measurements yield a value of about 10^{-4} mm of mercury for the pressure of the residual gas, exclusive of CO_2, at room temperature, and 0.97 as the average value of the reflectivity for the vacuum side of the silvered surfaces for temperature radiation of 300° K.

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I. INTRODUCTION

Vacuum jacketed vessels, or Dewar flasks, made of Pyrex glass are less subject to breakage than those made of soft glass, hence they are to be preferred for use as containers of liquefied gases and for the insulation of low-temperature apparatus. It has been difficult to obtain Pyrex flasks that have insulating properties equal to those of similar flasks made of soft glass. With the help of information collected from several sources and by modifications of the usual methods, a technique has been developed by means of which it is possible to produce Pyrex flasks of uniformly good insulating quality. The insulating properties of the silvered flasks prepared in the way described in this paper are such that even in the wide-mouthed cylin-

drical flasks filled with liquid air near to the lip, there is no boiling, the change of the liquid air to the gaseous phase taking place entirely by surface evaporation.

A description of the process finally used will be presented first, followed by a discussion of the method and the results of some tests.

II. PREPARATION OF THE SURFACES TO BE SILVERED

The space between the walls of the Dewar blank is filled with a potassium dichromate-sulphuric acid cleaning solution, and is maintained at a temperature of 60° C. for about 30 minutes. After removing the cleaning solution and rinsing with tap water, concentrated nitric acid is shaken in the flask for about 10 minutes. Finally, the flask is washed, first with tap water and then two or three times with distilled water. It is best to prevent the walls from getting dry by allowing distilled water to remain in the flask until ready to silver.

If the temperature of a silvered flask is raised rapidly preparatory to its evacuation at high temperatures, the silvering is usually spoiled. The silver becomes spotted and sometimes scales off the surface. Although it is preferable to raise the temperature slowly, the spoiling of the silvering with rapid heating can, to a large extent, be overcome by etching the glass before silvering. The inside surfaces to be silvered are etched slightly with a 0.7 molal solution of hydrofluoric acid before treating the surfaces with the concentrated nitric acid after the cleaning solution has been rinsed out. The hydrofluoric acid is allowed to remain in the flask for 10 minutes, during which time the flask is shaken occasionally. The hydrofluoric acid is rinsed out with tap water and a dilute solution of ammonia is shaken in the flask to neutralize any remaining traces of the acid.

III. SILVERING[1]

Although the Brashear process is used for silvering, the concentrations of the solutions and the proportions in which they are mixed have been modified.

Three solutions are prepared in the following proportions:

A. 2 L of distilled water + 50 g $AgNO_3$.

B. 2 L of distilled water + 90 g KOH.

C. (800 ml of distilled water + 80 g cane sugar) + (100 ml of alcohol + 3.5 ml HNO_3 specific gravity 1.42).

A should be kept in a dark place.

C improves with age.

The solutions are used in the proportions A:B:C = 16:8:1 by volume.

Concentrated ammonium hydroxide is added to solution A, drop by drop, while stirring, until the precipitate which first forms just completely disappears. To this is added the requisite amount of solution B, which causes a dark-brown or black precipitate to be formed. (If insufficient ammonium hydroxide was added before solution B was added, the precipitate will be yellowish green. If this occurs, the solution should be discarded and the process recommenced.) Ammonium hydroxide is added again, drop by drop, while stirring, until the

[1] For general information on silvering, the reader is referred to Bureau of Standards Circular No. 389, The Making of Mirrors by the Deposition of Metal on Glass, which can be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. Price, 5 cents.

black precipitate is almost, but not completely, dissolved. If the solution is allowed to stand for about 30 minutes it will clear up except for some black flakes which settle to the bottom. The solution may be used immediately after the last addition of ammonium hydroxide, although it can stand for as long as an hour without affecting the results.[2]

The solution is decanted into the flask through the evacuating tube, filling the space between the walls about two-thirds full. The required amount of C is added and the solutions are mixed by shaking. The flask should be shaken or rolled while the silver is being deposited.

The temperature of the solution is kept as near 15° C. as is practicable. The time required for the solution to react and deposit the silver on the glass walls depends, among other things, upon the age of the solution A; older solutions deposit silver more slowly. When A is more than one month old the rate of deposition may be very slow, but it can be increased by adding in the final precipitation and redissolving of the combined A and B solutions with ammonium hydroxide, a little less ammonium hydroxide than would ordinarily be added, or by adding a small amount of solution A after the end point has been reached. The time of completion of the silvering process is ascertained by occasionally pouring out a little of the solution and noticing the character of the precipitate. When the precipitate becomes flocculent, the silvering is completed, and the solution is removed quickly in order to prevent the formation of the gray deposit, or bloom, which appears in spent solutions. The time of silvering varies from 10 to 30 minutes. A second coat of silver may be deposited over the first after removing the spent solution and rinsing. It is advantageous to silver a flask a second time in this manner if an opaque coat is not obtained the first time. Brighter and thicker silver coats can be obtained with a given amount of the solutions by silvering twice with half the amounts (diluting with water if desired) than can be obtained by silvering once with the full amount. After the silvering is completed the solution is washed out and as much as possible of the sediment adhering to the walls is removed by a vigorous shaking of the flask about half full of water. After a final rinsing with distilled water, the flask is dried by alternately exhausting and filling with dry air.

IV. EVACUATING

The process used in evacuating and baking out the flasks was suggested by the results of some experiments of Langmuir [3] on evacuating and baking out incandescent lamps.

In order to out-gas a flask, silvered or unsilvered, it is heated to a temperature near the softening range. Unless precautions are taken some portion of the flask may reach the softening range and the flask be ruined. The chance that such overheating may take place increases with the size of the flask. It was found that it is advantageous to roll the flask in a sheet of copper on the outside of which is wrapped a sheet of asbestos paper about one-sixteenth inch thick. The flask

[2] There is danger of the formation of explosive compounds in ammoniacal silvering solutions after the addition of the reducing solution. This is discussed in Bureau of Standards Circular No. 289.

[3] Saul Dushman, Production and Measurement of High Vacuum, pp. 156-158. Publisher, General Electric Review, Schenectady, N. Y.

is then placed horizontally on some pieces of insulating brick in an electric furnace and connected to a high vacuum system equipped with a McLeod gauge capable of detecting a pressure of 10^{-5} mm of mercury. Any water remaining in the flask is removed by evacuation with the fore pump alone. When this is completed, the mercury diffusion pump is started and a trap between the flask and the rest of the vacuum system is cooled with liquid air to prevent the diffusion of mercury vapor into the flask and its amalgamation with the silver.

When the pressure has been reduced to a value too small to be read on the McLeod gauge, the furnace is heated to 550° C. Although the temperature of an unsilvered flask can be raised rapidly, the temperature of a silvered flask should be raised slowly, seven hours, at least, being allowed in reaching 550° C. It was found convenient in the laboratory to raise the temperature to about 400° C. on the day the out-gassing is started and to allow the flask to remain at this temperature over night, increasing it to 550° C. the next morning. If the temperature of an unetched silvered flask is raised too quickly the silver is usually spoiled and in many cases some of the silver comes off the glass. For unsilvered flasks and silvered ones that are etched before silvering, the whole baking out and sealing off process can be completed in seven hours. The temperature of the flask is determined with two thermocouples, one of which is placed inside the flask and the other between the flask and the copper sheet. The current through the furnace is adjusted until the temperature inside and outside the flask is 550° C., which should not be exceeded by more than a few degrees. Pumping is continued at this temperature for about an hour or until the pressure as read on the McLeod gauge shows no further decrease. The temperature is then allowed to fall to 400° C. and the pumping continued at this temperature for at least 30 minutes. Then the flask while still hot is sealed off.

Care must be taken in sealing off the flask to allow the gases evolved during the sealing off process to be pumped out before the seal is completed. The following description of the sealing off procedure is copied here from page 81 of the Production and Measurement of High Vacuum, by Dushman.

> Constrictions in glass vessels at points where they are to be sealed off after exhaust should not be too thick walled, otherwise a large body of glass will have to be heated during the seal off, causing the liberation of a great deal of gas. Furthermore, the constriction should be torched till it is almost melting and the pump allowed to exhaust the gas thus liberated for about two minutes, after which the sealing off should be performed as rapidly as possible without heating the glass any more than absolutely necessary.

The time required for removing the gases liberated before completing the seal will depend upon the size of the vacuum system and the speed of the pump. Four minutes were allowed for pumping out with the vacuum system used for this work.

After sealing off, the flask is removed from the furnace and cooled quickly in order to prevent further evolution of gases from the hot walls. This cooling may be effected by blowing air over the flask by means of an electric fan.

V. DISCUSSION OF THE METHOD

1. SILVERING

The silvering formula is the result of adjusting the proportions and concentrations of the reagents in the standard Brashear process. The conditions under which Dewar flasks are silvered are different from those generally met with in silvering mirrors. A difficulty which presents itself in the silvering of Dewar flasks is the removal through the small evacuating tube of the spent solution after the silvering is completed. This may require several minutes, during which time the silver surface tarnishes and a gray deposit, or bloom, collects on it. This bloom and tarnish form rapidly in solutions that deposit their silver quickly. The formula presented here is slow acting, so that the solution can be removed before there is any visible tarnishing and before an appreciable amount of bloom collects on the surface. It was also found that the appearance of the flasks silvered with the slow acting solutions recommended are in general better than those silvered with more rapidly acting solutions.

The recommended concentration of potassium hydroxide is the average of the lowest and highest concentrations which were found by trial to be just usable under the prevailing conditions. It was also found that adding sufficient ammonium hydroxide to completely clear up the first precipitate before the potassium hydroxide solution is added yielded more uniformly favorable results than additions of insufficient amounts.

Bureau of Standards Circular No. 389 recommends the addition of the potassium hydroxide directly to the silver nitrate solution, before adding any ammonium hydroxide. The same procedure may be used with the formula given in this paper, following the directions given in Circular No. 389 for clearing up the precipitate.

2. THE EFFECT OF HIGH TEMPERATURES ON SILVERED SURFACES

It frequently happens that heating a silvered surface in vacuo to a high temperature spoils its appearance. The silver becomes gray and appears to be thinner in parts and not infrequently scales off the glass. This, it has been found, is not due to any specific effect of the high temperature but is brought about by raising the temperature too rapidly. It can, to a large extent, be prevented by etching before silvering, but this is not necessary if the temperature is raised slowly enough. Before heating to a high temperature, the glass side of the silver coat of an etched Dewar flask is duller than that of an unetched flask, and although its appearance improves during the baking out, the outside appearance of the finished flask is not as good as that of the unetched flask. No difference was observed between the insulating properties of etched and unetched flasks.

In order to determine whether the high temperatures used in baking out flasks impair the reflectivity of the vacuum side of the silvered surface, which is the side effective in reducing heat transfer, eight glass plates, cut from a single larger plate of pyrex glass, were silvered and their reflectivities for visible light measured before and after heating in vacuo to high temperatures. The plates were silvered in a tray following as closely as possible the procedure used in silvering unetched flasks. The reflectivities for diffuse illumination of the

air side of the silver surfaces, which were simply dried and not rubbed or polished, were measured normal to the surfaces with a Martens photometer using a blue, a green, and a red filter.

The plates were placed in a glass tube and baked out at high temperatures: 4 at 500° C. for 3 hours, and the other 4 at 400° C. for 40 hours, after which these same 4 were baked out at 550° C. for 3 hours. The average values of the reflectivities of these 2 sets of 4 plates are given in Table 1.

TABLE 1

Filter	Reflectivity				
	Set I, 4 plates			Set II, 4 plates	
	Before baking	After baking for 40 hours at 400° C.	After an additional 3 hours at 550° C.	Before baking	After baking for 3 hours at 550° C.
Blue	0.34	0.42	0.57	0.36	0.59
Green	.56	.69	.79	.59	.82
Red	.75	.85	.92	.77	.94

These observations show that heating to a high temperature improves the reflectivity of the vacuum side of a silvered surface for visible light and that the higher the temperature, the higher the reflectivity becomes. Of course, it is the infra-red and not the visible spectrum that is important in determining the transfer of heat between the walls of a silvered flask, the wave length of maximum energy density for black body radiation at 300° K. being 9.6μ, but the measurements do make it seem very probable that if the high temperatures affect the reflectivity for 10μ radiation the result is an improvement rather than otherwise.

3. EVACUATION

The reasons for evacuating and baking out at 400° C. after a similar procedure at 550° C. are discussed by Dushman.[4] Briefly they are as follows: At temperatures near the softening range, glass undergoes marked changes and large quantities of gas diffuse from the interior out through the surface. While the gases are thus diffusing their concentration at the surface is large. If the flask is cooled rapidly from these high temperatures and sealed off, much of the gas at the surface is retained by the glass for a time, only to be given up slowly after sealing off. Although there is a small rate of diffusion from the interior of pyrex glass at 400° C., nevertheless gases at the surface can be effectively removed by baking for a short time at this temperature. It is not sufficient to remove only the gases adsorbed on the surface because, after sealing off, gases from the interior will diffuse slowly into the evacuated space.

Although the rate at which gases diffuse from the interior of glass at 400° C. is small as compared with the rate at 550° C., it is nevertheless appreciable, so that it is possible to produce good Dewar flasks by baking them out at 400° C. for long periods of time. In

[4] Saul Dushman—Reference cited.

a paper by Phipps, Copley, and Shaw [5] which appeared while this paper was being prepared for publication, baking out at 400° C. for 36 hours was recommended. It was decided to withhold publication until a comparison of the two methods could be made. This was done by preparing a number of silvered flasks, some by baking out at 550° and 400° C. as described above and the others at 400° C. for 40 hours. In order to eliminate differences due to a possible nonuniformity in the silver deposits, some of those baked out at 400° C. were afterwards baked out at 550° and 400° C. as recommended in this paper. In every case the flasks prepared by baking out at 550° C. and afterwards at 400° C. were slightly better. It was not determined whether this was because of a better vacuum or a possible improvement of the reflecting power of the silver at the higher temperature.

Baking out at the higher temperature has the further advantage that it requires less time which is especially favorable in the case of unsilvered and silvered flasks that have been etched. It has usually been considered that in baking out at temperatures above 400° C. there was danger in that the flask might collapse and that its silver coat would be impaired, but these troubles can be easily overcome by surrounding the flask with copper and asbestos, and by raising its temperature slowly or by etching.

VI. REFLECTIVITY OF THE SILVERED SURFACES AND DENSITY OF RESIDUAL GASES

In order to obtain approximate values of the reflectivity of the vacuum side of the silver deposit for temperature radiation, and the heat transferred by the residual gas between the walls, measurements were made of the rate of evaporation of liquid hydrogen and liquid air in a flask of about 1-liter capacity. These measurements made it possible to obtain separate values for the heat transferred by radiation and the heat transferred by the residual gas, since with liquid hydrogen in the flask the pressure of the residual gas is negligible and all the heat which crosses the vacuum space may be assumed to be transferred by radiation.

In order to reduce the flow of heat down from the lip, a flask with a long slender neck (15 cm long, 2.5 cm I. D.) was chosen. The flask was silvered and evacuated according to the process described above. The rate of evaporation was determined by measuring with a gas meter the volume of gas which evaporated during measured intervals of time. When the temperature of the outer wall was 29.5° C. liquid hydrogen evaporated at the rate of 3.0 g per hour and liquid air at the rate of 9.3 g per hour (period). For spherical flasks with long necks in which the residual gas pressure is small, of the order of 10^{-4} mm, the rate of evaporation was found to be independent of the depth of the liquid in the spherical bulb. This suggests that the entire inner bulb was approximately at the temperature of the liquid and that all the heat transferred across the vacuum space to the spherical bulb was absorbed by the liquid and subsequent computations were based on this assumption. The evaporated gases take up in the neck the major part of the heat which flows down from the lip and the heat which is transferred across the vacuum space

[5] T. E. Phipps, M. J. Copley, and E. J. Shaw, J. A. C. S., vol. 53, No. 4, p. 1365.

surrounding the neck. From a measurement of the temperature gradient along the inside neck of the flask an approximate value was obtained for the heat which flowed by conduction from the neck into the spherical bulb. It amounted to less than 5 per cent of the heat transferred to the spherical bulb by radiation and was considered small enought to be neglected in this approximate calculation.

When the flask was filled with liquid hydrogen the gas pressure between the walls was so small that the heat transferred by gas between the walls could be neglected. (At liquid hydrogen temperatures, it is estimated that the vapor pressure of nitrogen is of the order of 10^{-10} mm of Hg and that of oxygen is even lower.) Using the value 108 calories per gram as the latent heat of vaporization of liquid hydrogen the energy reaching the inner bulb of the flask was found to be 7.7×10^3 ergs per sec for each cm^2 of surface. Assuming that all this heat is transferred by radiation, the emissivity of the silvered surfaces may be calculated by the equation:

$$\frac{e\sigma}{2-e}(T_2^4-T_1^4)=A$$

where e = emissivity of the surface which is assumed to be independent of the temperature,

σ = Stefan-Boltzmann radiation constant $=5.72\times10^{-5}$ erg cm^{-2} $degree^{-4}$ sec^{-1},

T_1 = Absolute temperature of the inner surface $=20°$ K.,

T_2 = Temperature of the outer surface $=302.5°$ K.,

A = Energy absorbed per cm^2 of inner bulb, per sec $=7.7\times10^3$ ergs.

Substituting the values for the constants in the equation and solving for e, a value of 0.03 is obtained which corresponds to a reflectivity of 0.97 for temperature radiation of 300° K. The value found in the International Critical Tables for the reflectivity of a polished freshly prepared film for 10μ radiation is 0.99, which is the highest value found in these tables for the reflectivity of silver. Both to shorter and longer wave lengths the coefficient decreases a little.

Using the value 48.5 calories per gram as the latent heat of vaporization of liquid air, the heat transferred across the vacuum space when the flask contained liquid air was found to be 1.4 times as great as when the flask contained liquid hydrogen, the temperature of the outside surfaces of the flask being the same for both liquid air and liquid hydrogen. It is found therefore that about 29 per cent of the energy responsible for the evaporation of the liquid air was transferred by the residual gases.

Knowing the energy transferred by the residual gases when the flask was filled with liquid air, a calculation, based upon Knudsen's theory of the transfer of heat by rarified gases,[6] was made of the density of the residual gas, which was assumed to be principally nitrogen. Assuming an accommodation coefficient of unity, the density of the residual gas is found to be 1.2×10^{-10} g per cm^3 which corresponds to a pressure of 8×10^{-5} mm of Hg at room temperature. Assuming an accommodation coefficient of 0.9, which is more nearly the actual value, the density is 1.5×10^{-10} g per cm^3 and the corresponding

[6] L. B. Loeb, Kinetic Theory of Gases, Ed. 1, pp. 201-218. Publisher, McGraw Hill Book Co.

pressure at room temperature is 1.0×10^{-4} mm of Hg. The vapor pressure of carbon dioxide at liquid air temperature is about 6×10^{-6} mm of Hg. Consequently the percentage concentration of CO_2 at liquid air temperature is small but it is not possible to tell from these measurements what the concentration of CO_2 is at room temperature.

From these simple measurements and computations, one can see that it is not physically impossible to make better flasks than the one here described. If the reflectivity could be increased to 99 per cent, the highest value given in the International Critical Tables for any silver surface, and the vacuum could be made perfect, the rate of evaporation of liquid air would be reduced to about one-fourth of the value given above. In the case of liquid hydrogen the rate of evaporation would be about one-third of the value given.

VII. SUMMARY

A method has been described for silvering and evacuating Pyrex Dewar flasks by which it is possible to produce flasks with very good insulating properties equal to those of soft glass flasks.

VIII. ACKNOWLEDGMENTS

The authors take this opportunity to acknowledge the helpful suggestions made by Dr. M. F. Peters and F. A. Case.

WASHINGTON, July 29, 1931.

THE RELATION OF TORQUE TO TENSION FOR THREAD-LOCKING DEVICES

By H. L. Whittemore, G. W. Nusbaum, and E. O. Seaquist

ABSTRACT

This investigation was made to determine, under static loads, the torsional resistance to unscrewing of nuts, with and without locking devices, and the relationships these torques bear to the stresses in the bolt. The torque required to produce a given stress in the bolt was also determined for each device.

Twenty-four manufacturers of thread-locking devices accepted the invitation to submit samples of their device for test and agreed to publication of the results.

A total of 41 devices were tested, including such devices as standard nuts, jam nuts, and slotted nuts with cotter pins. Only about one-quarter of these devices showed any appreciable difference in the static torque-tension relation from that of the American National coarse-thread standard nut.

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I. INTRODUCTION

Screw threads are widely used to fasten parts of machines and structures. Where the parts are not subject to impact and vibration, a screw thread holds securely. However, where they are subject to impact, as in a railroad-track joint, or vibration, as in an automobile engine, ordinary nuts and bolts become loose and must be tightened frequently to prevent failure. For this reason devices are used to

lock the screw threads. Thousands of patents have been issued for devices of this kind, and there are many now on the market.

The importance of this problem to the industries and the people of this country led the Bureau of Standards to undertake an investigation of methods of locking screw threads, to determine, if possible, the properties of different locking devices under conditions simulating those found in service.

A search through the technical literature gave very little information. In fact, no article bearing specifically on the problem of locking screw threads was found. No complete experimental investigation of the standard theory, developed by Persy [1] for the effect of friction on the torque-tension relationship of ordinary nuts, was found, although a few authors [2–9] have determined screwing-on torques for a number of regular nuts.

A few tests of thread-locking devices have been made by commercial organizations and the results used by them. A study of the reports of tests of this kind which were available showed none that could be used as a basis for generally valid conclusions, because in no case was an attempt made to measure the forces acting on the locking device during the test, or to evaluate the significace of the other variables which have an effect on the results. For example, if one locking device is used in an air hammer, then replaced by another device, the fact that one of the devices loosened and the other did not would not prove the superiority of the one which did not loosen unless the forces which acted on each device had been measured and found to be the same. An assumption that the forces were the same on both devices may lead to serious errors. The measurement of forces exerted upon a machine part subjected to impact and vibration is one of the most difficult problems in mechanical testing, and one for which, in many cases, methods and apparatus have not been developed.

A program for the investigation was therefore outlined, planned to analyze the forces acting on screw threads which tend to unscrew them and to study the behavior of different thread-locking devices subjected to the action of these forces under measured conditions. All known manufacturers of devices for preventing the unlocking of screw threads; that is, for preventing the rotation of the nut on a bolt—were invited to cooperate in this investigation by submitting samples of their devices.

Other things being equal, a locking device requiring a high torque to unscrew it would be expected to prove more satisfactory in service than one requiring a low torque. A part of this program, therefore, consisted of a study of the torque required to screw on and screw off each locking device under static conditions. Because the conditions

[1] J. V. Poncelet, Frottement des vis et des écroux, Crelle's Journal, vol. 2, pp. 293–300, 1827. See also F. Grashof, Maschinenlehre (Voss, Leipzig, 1883), vol. 2, pp 265–276.
[2] H. Camerer, Beiträge zur Schraubenberechnung, Zeits. des V. D. I., vol. 44, pp. 1063–65, Aug. 11, 1900.
[3] Carl Stimson, Test of Track Bolts and Wrenches, Proceedings of the American Railway Association, vol. 17, pp. 265–280, 1916.
[4] Oberhuber and Abele, Bolts for Use in Power Plant Construction, Mechanical Engineering, vol. 48, pp. 500–504, May, 1926.
[5] George S. Case, Stresses on Bolts—Nut Dimensions—Wrench Design, Mechanical Engineering, vol. 48, pp. 919–925, September, 1926.
[6] W. Köhler, Anzugspannungen und deren bedeutung bei der arbeit der schraube, Bergmann Mitteilungen, vol. 4, pp. 223–229, November–December, 1926.
[7] Résistance et pose des vis et des boulons; proportions des écroux et des clés, Pratique des Industries Mecaniques, vol. 12, pp. 105–109, June, 1930.
[8] K. Schimz, Eine neue statische schraubenprüfmaschine, Maschinenbau, vol. 9, pp. 573–575, Sept. 4, 1930.
[9] Albert Kingsburg, Experiments on the Friction of Screws, Trans. Am. Soc. Mechanical Engineers, vol. 17, pp. 96–116; 1896.

in these tests were more readily controlled and measured, this part of the program has been completed first.

The development of apparatus for determining the behavior of these devices under other measured conditions, particularly conditions more closely simulating those which occur in service, has made considerable progress, and additional reports will be published when data have been obtained which warrant publication.

This report is, then, the first of the reports on this investigation of devices for locking screw threads. It gives a drawing and description of each of the locking devices submitted by the cooperating manufacturers; a description of the apparatus and methods used for determining the relation between the screwing-on and screwing-off torques on the nut and the tensile stress in the bolt. The results of the tests are given in a series of curves, and some general conclusions have been drawn. A fuller coordination of the experimental results and theory will be attempted when the investigation has progressed further.

II. SCOPE OF THE INVESTIGATION

Forty-one devices were included in the investigation and are described in detail under III, Specimens. Twenty-four manufacturers submitted 33 locking devices from commercial stock. Some of these devices were ordinary [10] nuts which had been modified, and one was an ordinary bolt which had been modified; that is, they had features not found in ordinary nuts and bolts. These will hereafter be referred to as "modified" nuts and "modified" bolts. Of these 33 locking devices 16 were modified nuts, one was a modified bolt, and two had a special thread for both bolt and nut. Fourteen were separate devices to be used with ordinary nuts, of which 10 were spring or lock washers. With all of these separate devices U. S. standard regular nuts were used.

In addition to the locking devices submitted by the manufacturers, the test program included the following ordinary devices: American National coarse-thread regular nut, American National fine-thread regular nut, each of these nuts with jam nuts, and American National fine-thread castellated nut with cotter pin. American National coarse-thread slotted or castellated nuts with cotter pins would have been included in the program if they could have been obtained commercially.

Because the older U. S. standard nuts are still extensively used there were also included tests on U. S. standard regular nuts, U. S. standard regular nuts with jam nuts, and U. S. standard slotted nuts with cotter pins.

As it was considered desirable to make all of the tests on devices of the same nominal size, all bolts had a nominal diameter of three-fourths inch. This size was considered representative of the screw threads widely used in engineering work. For the same reason, all bolts had the American National right-hand coarse thread except those used with American National fine-thread nuts and with the two devices having a special thread.

The dimensions of the American National thread (coarse and fine) nuts and bolts are given in the Report of the National Screw Thread

[10] American National and U. S. standard nuts will hereafter be referred to as "ordinary nuts" and American National bolts as "ordinary bolts."

Commission, Bureau of Standards Miscellaneous Publication No. 89, and those of the U. S. standard thread in the Report of the Special Committee on a Uniform System of Screw Threads, Journal of the Franklin Institute, volume 49, pages 53–57, 1865 (adopted March 16, 1865, l. c., p. 280).

The ¾-inch American National coarse thread has 10 threads per inch. The regular nut is $^{21}/_{32}$ inch thick and 1⅛ inches across flats of the hexagon. The jam nut is $^{7}/_{16}$ inch thick. The American National fine thread has 16 threads per inch. The regular nut and the jam nut are the same sizes as the coarse-thread nuts.

The U. S. standard thread, like the American National coarse thread, has 10 threads per inch, but the regular nut is larger, being ¾ inch thick and 1¼ inches across the flats of the hexagon. The U. S. standard does not prescribe the dimensions of jam nuts. The jam nut was, therefore, made $^{7}/_{16}$ inch thick, the same as for the American National nut. The differences between the American National coarse thread and the U. S. standard thread are so small that a U. S. standard nut may be used on an American National coarse-thread bolt.

III. SPECIMENS

1. DEVICES

To each device a symbol was assigned, viz: *I*, *II*, *III*, etc., for non-proprietary devices; A, B, C, etc., and AA, BB, CC, etc., for proprietary devices; of these the devices designated by double letters were spring washers.

A description (and for the devices designated by letters a drawing to scale) of each device follows. Unless otherwise noted in the description, the device was made of steel.

Device *I* was an American National coarse-thread regular nut.

Device *II* was a U. S. standard regular nut.

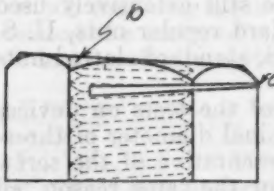
Device *III* was an American National fine-thread regular nut.

Device *IV* was an American National coarse-thread regular nut and a jam nut.

Device *V* was a U. S. standard regular nut and a jam nut.

Device *VI* was an American National fine-thread regular nut and a jam nut.

Device *VII* was a U. S. standard slotted nut and a cotter pin, ⅛ inch in diameter. The slots in the nut were $^{5}/_{16}$ inch wide and ¼ inch deep.



A

FIGURE 1.—*Device A*

Device *VIII* was an American National fine-thread castellated nut and a cotter pin, ⅛ inch in diameter. The slots in the nut were $^{5}/_{32}$ inch wide and ¼ inch deep. The width across the flats of the hexagon measured 1$^{1}/_{16}$ inches, being less than the standard dimension, which was 1⅛ inches.

Device A, Figure 1, was a U. S. standard nut, slotted and then permanently deformed so as to close the slot at *a*. One thread had been removed at *b* for an arc of approximately 60°. When the device was screwed on a standard bolt, the slot in the nut was forced open at *a*, causing the threads in the nut to exert forces upon the threads of the bolt, which increased the frictional resistance to rotation of the nut.

Device B, Figure 2, was a bolt and nut having a special thread, eight threads per inch. The sides of the threads were symmetrical and had an included angle of 29°, the same as the Acme thread. The surfaces at the major diameter of the bolt and nut were cylindrical. The surfaces at the minor diameters were tapered, forming a screw helicoid having a small angle with the axis, hereafter referred to, for simplicity, as helical cones. When the nut was screwed on the bolt it had the

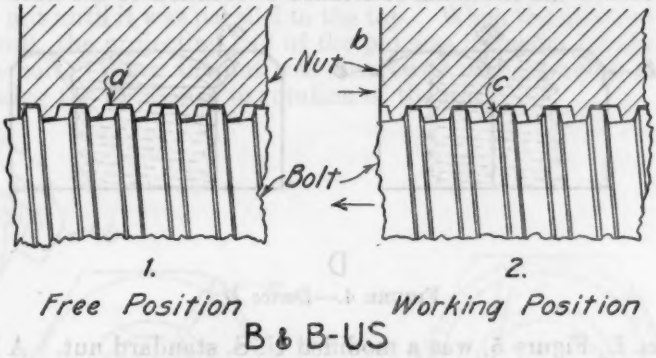


FIGURE 2.—*Devices B and B–U. S.*

position shown at 1, there being a space, *a*, between the threads of the bolt and the nut. In this position the nut rotated freely. When the nut was tightened, the force on the bearing face, *b*, of the nut first brought the helical cones together, then increased the elastic compression on these cones until the thrust faces, *c*, came into contact. When the stress in the bolt reached the working value, much of the load was carried by these thrust faces of the threads. The helical cones in the nut exerted compressive forces on the cones on the bolt, increasing the frictional resistance of the nut to rotation.

The nuts were $^{27}/_{32}$ inch thick and 1⅛ inches (the same as American National) across the flats of the hexagon.

Device B–U. S., Figure 2, was identical with B except that the nut was 1¼ inches (the same as U. S. standard) across the flats of the hexagon.

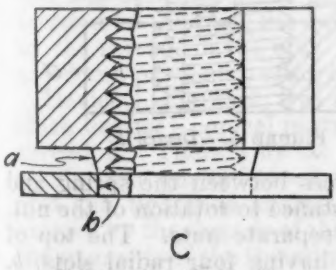


FIGURE 3.—*Device C*

Device C, Figure 3, consisted of a malleable iron nut and a punched steel washer. The nut had a conical projection, *a*, extending from its bearing face. The small diameter of this cone fitted into the bore of the washer, *b*. As the nut was tightened, the conical projection was forced into the washer, thereby compressing the cone and increasing the forces exerted by the threads in this portion of the nut on the threads of the bolt. Thus the frictional resistance of the nut to rotation was increased. Except for the threads, the nut was not machined. The nut was $^{29}/_{32}$ inch thick over all and 1¼ inches across the flats of the hexagon.

Device D, Figure 4, was a modified U. S. standard nut with two diametrically opposite radial slots, *a*. The nut had been permanently deformed by compressive forces having the action lines, *b*—*b*. When the device was screwed on a standard bolt it rotated freely until the deformed portion of the nut reached the end of the bolt. Continued rotation forced the deformed threads of the nut against the bolt threads. The forces which these deformed threads exerted on the bolt increased the frictional resistance to rotation of the nut.

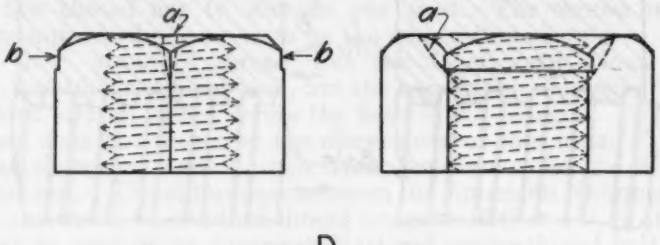


FIGURE 4.—*Device D*

Device E, Figure 5, was a modified U. S. standard nut. A helical spring, *a*, having about two coils of steel wire 0.081 inch diameter, was placed in a recess in the bearing face of the nut. One end of the spring was bent parallel to the axis of the coil and inserted in a hole, *b*, at the bottom of the recess to prevent rotation of the spring with respect to the nut. When the nut was screwed on a standard bolt, the bolt first engaged the coil spring and then the thread of the nut. The frictional forces between the spring and the bolt increased the diameter of the spring as the nut was screwed on the bolt. If the nut was unscrewed, the frictional forces decreased the diameter of the

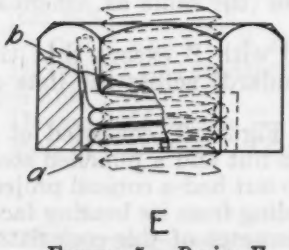


FIGURE 5.—*Device E*

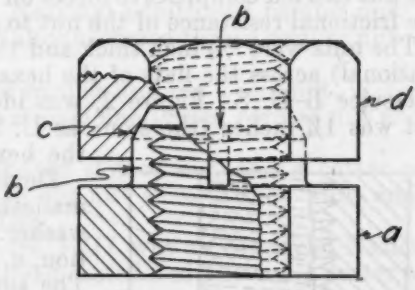


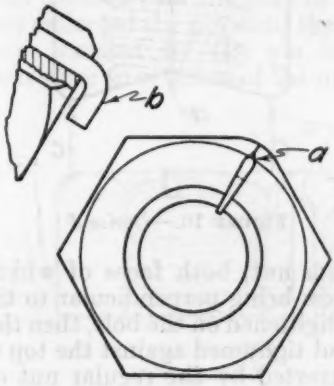
FIGURE 6.—*Device F*

spring, thus increasing the frictional forces between the spring and the bolt and increasing the frictional resistance to rotation of the nut.

Device F, Figure 6, consisted of two separate nuts. The top of the first nut, *a*, consisted of a cylinder having four radial slots, *b*. The top end of the cylinder had a conical surface, *c*. The jam nut, *d*, had a conical recess in its bearing face. Nut *a* was first screwed on the bolt and tightened. Nut *d* was then screwed on the bolt and tightened. The forces exerted at *c* by the tapered recess in nut *d* on the conical portions of nut *a* increased the forces exerted by the threads in the cylindrical portion of nut *a* upon the threads of the

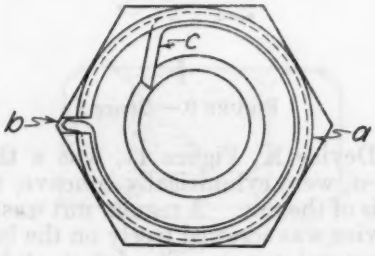
bolt and increased the frictional resistance to rotation of the nuts. Both nuts were 1¼ inches across the flats of the hexagons. The thickness of the first nut was 13/16 inch over all and that of the jam nut ⅝ inch. The recess in the jam nut was 5/16 inch deep. The total thickness of threaded portions of the two nuts was 1⅛ inches.

Device G, Figure 7, was a modified U. S. standard nut. The top had a hole, *a*, in which a pin, *b*, was a tight fit. The portion of the pin which projected from the top of the nut was bent toward the axis of the nut until it was parallel to the top. When the nut was screwed on a bolt, the projecting end of the pin was deflected by the threads on the bolt. When the nut was unscrewed, the pin acted as a pawl, increasing the resistance to rotation of the nut.



G

FIGURE 7.—*Device G*



H

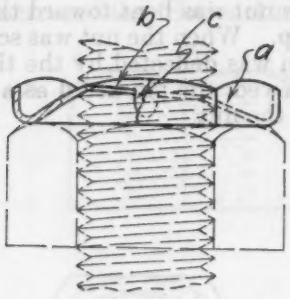
FIGURE 8.—*Device H*

Device H, Figure 8, was a nut with an annular groove, *a*, in a recess in the top. The wall of the recess had a radial slot, *b*. A wire spring, *c*, was sprung into the groove, *a*. One end of the spring was bent radially outward and was restrained by the slot, *b*, and the other end was bent inward to engage the bolt thread. When the nut was screwed on the bolt, the inner end of the spring was deflected outward by the threads of the bolt. When the nut was unscrewed, the spring acted as a pawl, increasing the resistance to rotation of the nut.

Device I, Figure 9, was a jam nut made from sheet steel 0.043 in. thick having a conical portion, *a*, the inner edge of which was a single thread, *b*. There were six radial slots, *c*, in the inner edge. After a regular nut was tightened on the bolt this device was screwed on the bolt and tightened against the top of the regular nut. The forces, exerted by the threads of the bolt on the thread of this device, deflected the segments of the thread inward against the roots of the bolt threads, increasing the frictional resistance to rotation of the nut. The distance across the flats of the hexagon was 1 3/32 inch.

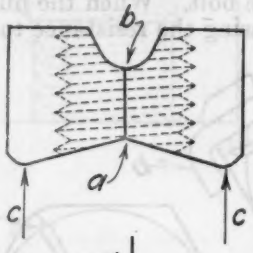
Device J, Figure 10, was a special nut having a shallow V-shaped groove, *a*, extending diametrically across the bearing face. A deeper and narrower groove, *b*, parallel to *a*, extended diametrically across

the top. The nut rotated freely on the bolt until the bearing face came into contact with the part to be clamped. Tightening the nut caused forces to be exerted at *c*—*c* in the direction of the arrows. These forces deformed the nut and increased the frictional resistance to rotation of the nut. The nut was 1⅛ inch thick and 1¼ inches across the flats of the hexagon.



I

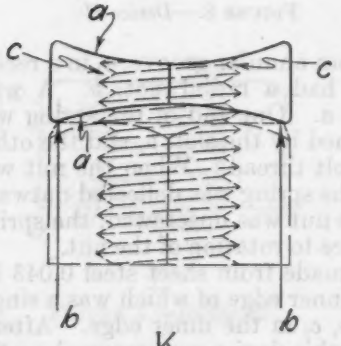
FIGURE 9.—*Device I*



J

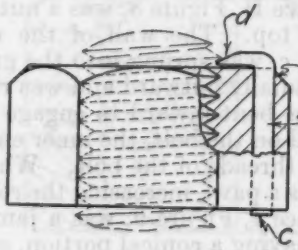
FIGURE 10.—*Device J*

Device K, Figure 11, was a thin jam nut, both faces of which, *a*—*a*, were cylindrically concave, the axes being perpendicular to the axis of the nut. A regular nut was first tightened on the bolt, then this device was screwed freely on the bolt and tightened against the top of the regular nut. The forces at *b*—*b* exerted by the regular nut on this device deformed it, thereby increasing the forces at *c*—*c* upon the bolt threads. These latter forces increased the frictional resistance



K

FIGURE 11.—*Device K*



L

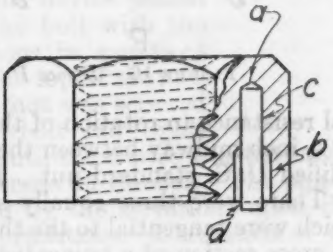
FIGURE 12.—*Device L*

to rotation of this device. The nut was 1¼ inches across the flats of the hexagon. The thickness at the outer edges was 7/16 inch. The minimum thickness was 5/16 inch.

Device L, Figure 12, was a modified American National coarse-thread nut having a hole, *a*, parallel to the axis. A pin, *b*, was a snug fit in this hole. The end, *c*, of this pin projected 0.01 to 0.02 inch from the bearing face of the nut and the other end, *d*, extended inward,

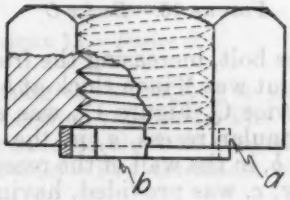
radially, to the minor diameter of the threads of the nut. When the nut was screwed on the bolt, it rotated freely until the end, *c*, of the pin came into contact with the part to be clamped. As the nut was tightened, the pin was pushed toward the end of the bolt, causing the end, *d*, of the pin to exert forces on a thread of the bolt, which increased the frictional resistance to rotation of the nut.

Device M, Figure 13, was a modified U. S. standard nut with a hole, *a*, in the bearing face, parallel to the axis. This hole had a counterbore at *b*. A hardened taper pin, *c*, 0.122 inch diameter at the outer edge, was a snug fit in the hole, the end, *d*, extending 0.03 to 0.04 inch beyond the bearing face of the nut. When the nut was screwed on the bolt it rotated freely until the end, *d*, of the pin came into contact with the part to be clamped. Further tightening of the nut deflected the pin until the face of the nut came into bearing. The force exerted by the pin in its deflected position increased the resistance to rotation of the nut.



M

FIGURE 13.—*Device M*



N

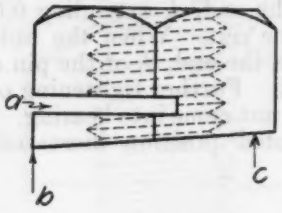
FIGURE 14.—*Device N*

Device N, Figure 14, was a modified U. S. standard nut with a cylindrical recess, *a*, in the bearing face. A soft copper ring, *b*, formed from a rectangular strip with butted ends, fitted into the recess and extended beyond the face of the nut. The inner diameter of the ring was slightly larger than the bolt. When the nut was screwed on the bolt it rotated freely until the ring came into bearing with the part to be clamped. Further tightening of the nut deformed the ring, which flowed into the bolt threads. The forces exerted by the ring on the bolt threads and on the recess in the nut increased the frictional resistance to rotation of the nut.

An alternative method of using this device is to screw it on the bolt so that the recess and copper ring are in the outer face. After the nut is tightened, the ring is deformed by a suitable tool and hand hammer. This method was not used in this investigation.

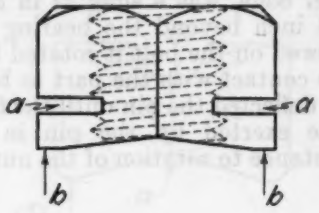
Device O, Figure 15, was a modified U. S. standard nut with a slot, *a*, which extended ⅛ inch beyond the axis. The bearing face was beveled so that the greatest thickness of the nut was along the outer edge of the slot at *b*. As the nut was tightened on the bolt, a force was exerted at *b* in the direction of the arrow, bending the portion of the nut below the slot, thereby increasing the forces on the threads of the bolt. These forces increased the frictional resistance to rotation of the nut. The thickness of the nut at *b* was ¼ inch and at *c* was ⅛ inch.

Device P, Figure 16, was a modified U. S. standard nut with two parallel slots, *a*—*a*, one in each of two opposite sides of the hexagon, extending to the minor diameter of the threads. There was a shallow V-shaped groove diametrically across the bearing face in such a position that the thickest portions, *b*—*b*, of the nut were along the open edges of the slots. When the nut was tightened on the bolt, forces were exerted at *b*—*b* in the direction of the arrows which deformed the nut and increased the forces which the threads in the nut exerted



O

FIGURE 15.—*Device O*

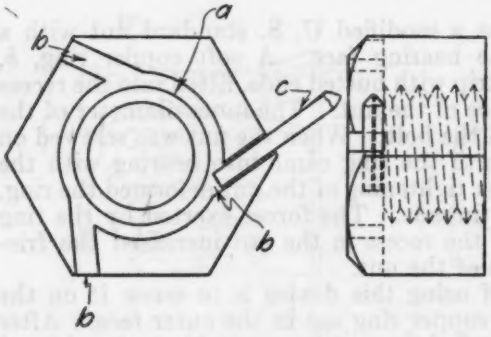


P

FIGURE 16.—*Device P*

on the bolt, increasing the frictional resistance to rotation of the nut. The nut was ¼ inch thick at *b* and 1/16 inch midway between the slots.

Device Q, Figure 17, was a modified U. S. standard nut. It had an annular recess, *a*, in the top. There were three equally spaced slots, *b*, in the wall of the recess, which were tangential to the threads. A key, *c*, was provided, having the cross section of a truncated equilateral triangle whose height was 0.117 inch and whose width of base was 0.131 inch. After the nut was screwed on the bolt and tightened, the key was placed in one of the slots and driven between the wall of the recess and the bolt threads, thus bending the key around the bolt threads. The forces exerted by the key upon the nut and upon the threads of the bolt increased the frictional resistance to rotation of the nut.



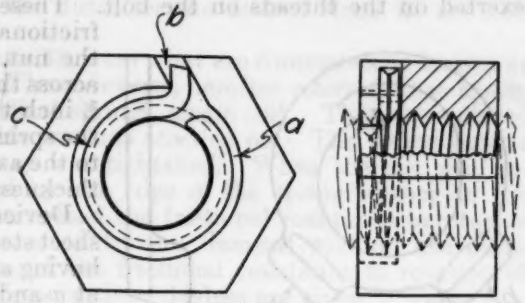
Q

FIGURE 17.—*Device Q*

Device R, Figure 18, was a modified U. S. standard nut. It had a recess, *a*, in the bearing face. A slot, *b*, tangential to the threads, extended from one of the sides of the nut through the wall of the recess. A single coil helical spring, *c*, was provided, having the cross section of a truncated equilateral triangle, whose height was 0.098 inch and width of base was 0.11 inch. One end of this spring extended radially outward. The spring was screwed on the bolt for one thread. The nut was then placed over the spring and the nut and spring were then rotated together. An axial force had to be

applied to the nut until it engaged the bolt threads, after which the nut and spring acted as a unit. As the nut was screwed on the bolt, the frictional forces between the spring and the bolt caused the diameter of the coil of the spring to increase. When the direction of rotation of the nut was reversed, the diameter of the coil of the spring was decreased, increasing the forces between the spring and the bolt, which increased the frictional resistance to rotation of the nut.

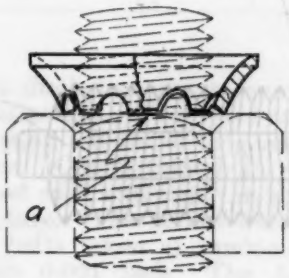
Device S, Figure 19, was a conical soft steel washer having serrations, *a*, in the inner edge. A regular nut was first tightened on the bolt and this device placed over the bolt with the serrations in contact with the top of the nut. A jam nut was screwed on the bolt and tightened until the device was flattened, causing the serrations to engage the threads on the bolt. The jam nut was then removed. The forces exerted by the serrations upon the threads of the bolt caused frictional resistance to rotation of the device. The thickness of the washer was 0.083 inch.



R

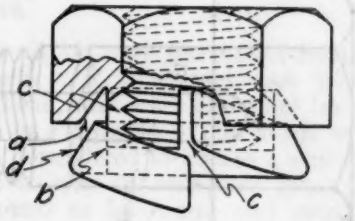
FIGURE 18.—*Device R*

An alternative method of applying this device is to flatten the device, using a suitable piece of tubing, by blows of a hand hammer. This method was not used in this investigation.



S

FIGURE 19.—*Device S*

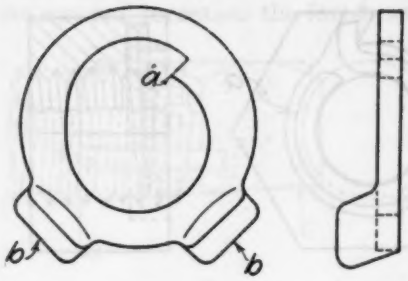


T

FIGURE 20.—*Device T*

Device T, Figure 20, consisted of a special nut and a helical steel spring washer. The nut had a conical seat, *a*, in the bearing face and a cylindrical portion, *b*, extending from the bottom of the conical seat outward beyond the face of the nut. This cylindrical portion had two diametral slots, *c*, perpendicular to each other. The outside of the spring washer, *d*, was conical and the inside was cylindrical. The washer was placed in the recess, then the nut was screwed freely

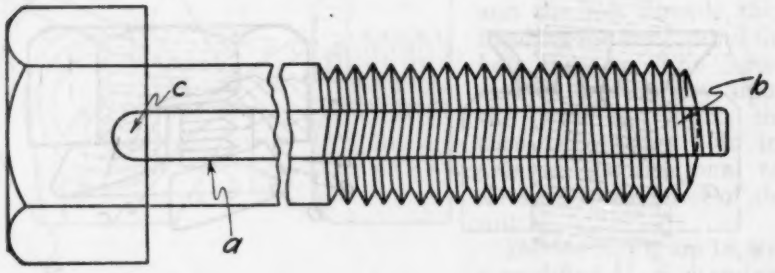
on the bolt until the washer came into bearing with the part to be clamped. Tightening the nut compressed the washer against the concial seat in the nut. The forces exerted by the conical seat in the nut decreased the diameter of the washer and exerted compressive forces upon the segments of the cylindrical portion, *b*, thus increasing the forces which the threads in the cylindrical portion of the nut exerted on the threads on the bolt. These last forces increased the frictional resistance to rotation of the nut. The nut was 1 5/16 inches across the flats of the hexagon and ¾ inch thick. The dimensions of the spring were 0.201 inch parallel to the axis and 0.281 inch in radial thickness.



U

FIGURE 21.—*Device U*

Device U, Figure 21, was a soft sheet steel washer, 0.138 inch thick, having a sharp prong in the bore at *a* and two lugs, *b*, on the outer edge making an angle of approximately 80° with the face of the washer. The washer was placed on the bolt under a regular nut, with the lugs adjacent to the sides of the nut. The nut was then screwed freely on the bolt. When the nut was tightened the washer turned with it until it came into bearing. The prong in the washer was then forced into the threads of the bolt by the forces which the corner of the nut exerted on the lugs. The force exerted by the prong on the threads of the bolt increased the frictional resistance to rotation of the washer. Since only a small rotation of the nut with respect to the washer was permitted by the lugs, the resistance of the nut to rotation was also increased.



V

FIGURE 22.—*Device V*

Device V, Figure 22, was a bolt having a keyway extending the full length of the shank and into the head. The bolt was threaded with an American National right-hand thread. A steel key, *a*, fitted snugly in the keyway. This key had notches, *b*, in its outer surface for a length corresponding to the length of the bolt threads. The notches near the end of the bolt matched those on the bolt, but the lead angle changed gradually to that of a left-hand thread. The

end of the key, *c*, in the head of the bolt was L-shaped, so that, when it came into bearing, axial movement of the key was prevented. A regular nut screwed on the bolt freely for the first few threads. As the nut was tightened, the forces exerted on the key notches increased the frictional resistance to rotation of the nut. Additional resistance to rotation was provided by bending the free end of the key sharply over the top of the nut after the desired stress in the bolt was obtained.

Devices AA to JJ, Figure 23, were what are commercially known as lock or spring washers. These devices, herafter referred to as spring washers, were all steel helical springs, single coil. They were placed on the bolt, then a regular nut was screwed on. The spring washer was compressed as the nut was tightened. When the nut was unscrewed the force exerted by one edge of the spring washer on the bearing face of the nut increased the frictional resistance to rotation of the nut. The force exerted by the clamped part on the other edge of the washer increased the frictional resistance to rotation of the washer. The dimensions of these devices are given in Table 1.

TABLE 1.—*Dimensions of spring washers*

Devices AA to JJ

Device	Thickness parallel to axis	Width at right angle to axis	Remarks
	Inch	*Inch*	
AA	1/4	1/4	
BB	7/32	11/32	
CC	1/4	3/8	
DD	5/16	3/8	Outside edge rounded, inside surface knurled.
EE	5/16	1/4	Inside and outside knurled.
FF	7/32	1/4	Both faces knurled radially.
GG	1/8	1/4	Ends of coil wedge-shaped.
HH	5/16	1/4	Do.
II	7/32	3/8	Do.
JJ	5/16, 9/32	5/16	Wedge-shaped rib adjacent to bore on one side.

2. BOLTS

All the bolts, except device V, Figure 22, were purchased for this investigation. They were made from S. A. E. 1020 steel, were ¾ inch diameter, 8.0 inches long under the head, and were threaded for 2½ inches. One of these bolts is shown in Figure 24. The heads were formed cold, and then the bolts were normalized to obtain a uniform structure. The bodies were ground to size on centerless grinders. Ten bolts taken at random were found to be round and straight within 0.001 inch. The American National coarse threads were ordered to meet the specifications for class 2, Free fit. The American National fine threads were ordered to meet the specifications for class 3, Medium fit. Measurements showed that they complied with these requirements. The bolts for devices B and B–U. S. were threaded by the manufacturer of the device.

From three bolts taken at random, American Society for Testing Materials standard tensile specimens were machined, having a diameter of ½ inch and a gage length of 2 inches. The Vickers number was determined upon 40 bolts using a diamond pyramid indenting tool and a load of 30 kg. Mechanical properties of the bolt material are given in Table 2.

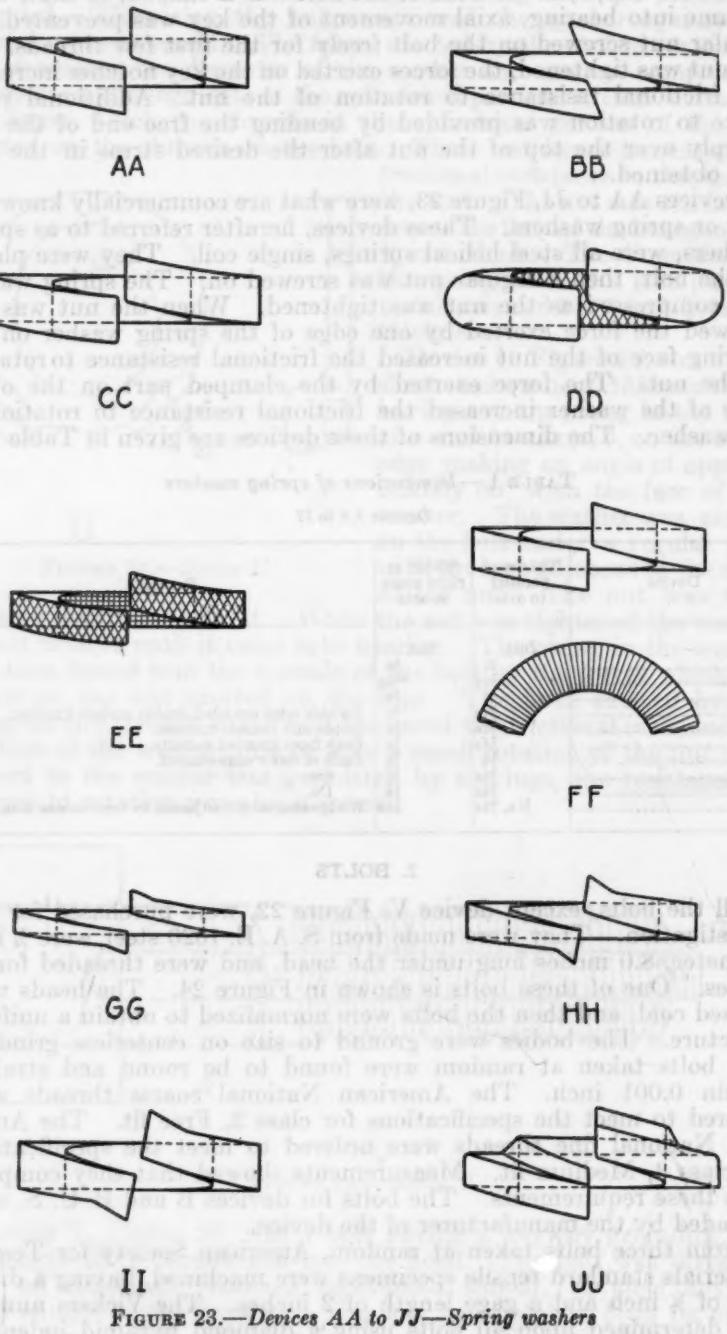


FIGURE 23.—*Devices AA to JJ—Spring washers*

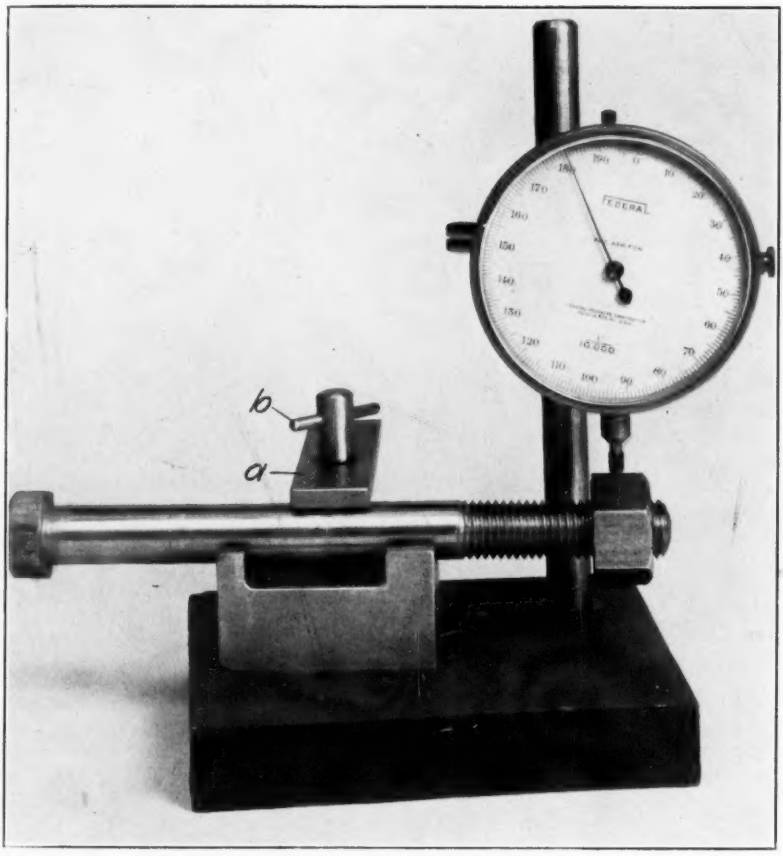


FIGURE 24.—*Fixture for measuring the clearance between the threads on the bolt and the threads in the nut*

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TABLE 2.—*Mechanical properties of bolt material*

Specimen	1	2	3	Average
Limit of proportionality, lb. per sq. in.[1]	51,500	43,100	51,500	48,700
Yield point, lb. per sq. in.[2]	60,000	54,800	59,200	58,000
Ultimate strength, lb. per sq. in.	71,000	66,800	73,200	70,400
Young's modulus of elasticity, lb. per sq. in.	28,700,000	28,500,000	29,500,000	28,900,000
Elongation in 2 inches, per cent	27	27	27.5	27.2
Reduction in area, do	64.7	64.3	57.3	62.1
Vickers number [3]				167

[1] Determined as the stress at which the stress-strain curve deviated from a straight line by 0.00001 inch per inch.
[2] Determined by drop of beam.
[3] Maximum, 191; minimum, 146.

3. ORDINARY NUTS

The regular nuts were American National coarse thread, American National fine thread, and U. S. standard. They were all (except those used with device V, which were furnished by the manufacturer) made from S. A. E. 1112 cold-rolled hexagon steel and were classed commercially as "semifinished" nuts. The slotted and castellated nuts were purchased from commercial stock. All of the other nuts were supplied by the manufacturer of the device.

4. VICKERS NUMBERS

The Vickers number of each locking device is shown in Table 3, the value given representing the mean of nine indentations, using a diamond pyramid (three indentations on each of three specimens). The load used (10, 30, or 50 kg) was chosen to give an impression which could be easily measured. The regular nuts showed little variation, the maximum deviation from the mean being 4.2 per cent. The modified nuts were somewhat less uniform, showing deviations from the mean as great as 13 per cent. The spring washers showed deviations as high as 12 per cent. Variations of these magnitudes are to be expected in good commercial practice. There was no indication that these variations had any effect upon the torque tension relationships of any of the devices.

TABLE 3.—*Vickers numbers of locking devices*

Device	Load	Vickers number		
		Maximum	Minimum	Average
	kg			
I. American National coarse-thread regular nut	50	222	205	213
II. U. S. standard regular nut	50	208	200	203
III. American National fine-thread regular nut	50	214	209	212
IV. American National coarse-thread regular nut and a jam nut	50	222	205	213
V. U. S. standard regular nut and a jam nut	50	208	200	203
VI. American National fine-thread regular nut and a jam nut	50	214	209	212
VII. U. S. standard slotted nut and a cotter pin	50	228	217	221
VIII. American National fine-thread castellated nut and a cotter pin	50	229	222	225
A	30	174	161	167
B, Nut	30	138	132	135
Bolt	30	191	146	167
B–U. S., Nut	30	145	129	137
Bolt	30	191	146	167

TABLE 3.—*Vickers numbers of locking devices*—Continued

Device	Load	Vickers number		
		Maximum	Minimum	Average
	kg			
C, Nut	30	145	125	132
Washer	30	131	127	129
D	30	176	157	164
E, Nut	30	203	197	200
Spring	50	516	497	503
F, Bottom nut	50	213	210	212
Top nut	50	213	204	210
G, Nut	50	225	223	224
Spring	50	492	479	486
H, Nut	50	211	197	204
Spring	50	579	536	556
I	50	371	348	358
J	30	147	116	134
K	30	165	150	157
L, Nut	30	160	157	159
Pin	50	541	516	531
M, Nut	50	212	209	211
Pin	50	450	423	435
N, Nut	50	214	209	211
Copper ring	10	91	66	81
O	30	212	192	200
P	30	177	164	172
Q, Nut	50	215	213	214
Key	50	328	325	326
R, Nut	50	215	207	211
Spring	50	571	254	465
S	30	149	146	148
T, Nut	50	214	207	211
Spring	50	455	422	442
U	30	166	115	148
V, Nut	50	223	186	209
Key	30	195	169	184
Bolt	30	189	163	180
AA	50	488	458	468
BB	50	541	479	504
CC	50	546	526	533
DD	50	458	438	450
EE	50	541	536	539
FF	50	466	396	437
GG	50	454	423	446
HH	50	497	402	458
II	50	488	470	478
JJ	50	531	466	509

IV. TESTING EQUIPMENT

1. TORQUE-TENSION MACHINE

The torque-tension machine was designed for this investigation and is shown in Figures 25 and 26.

The pendulum axle, *a*, was mounted in the frame, *b*, on ball bearings, *c*, so that it rotated freely. The bolt, *d*, rotated with the axle of the pendulum, the head being locked to the axle by a wedge-shaped collet, *e*, hexagonal inside and outside. In the other end of the axle was an annular recess, *f*, into which the replaceable bearing washer, *g*, fitted snugly. This washer was keyed to the axle so that it rotated with it. These washers had a Vickers number of 200 when indented with a diamond pyramid under a load of 30 kg. The locking device, *h*, was screwed on the bolt until the face of the device came into contact with the washer. Surrounding the device was the driving sprocket, *i*, rotating on the same axis as the axle of the pendulum. This sprocket could be rotated in either direction by the manually operated mechanism, *j*. A coupling, *k*, connected the driving sprocket with the locking device.

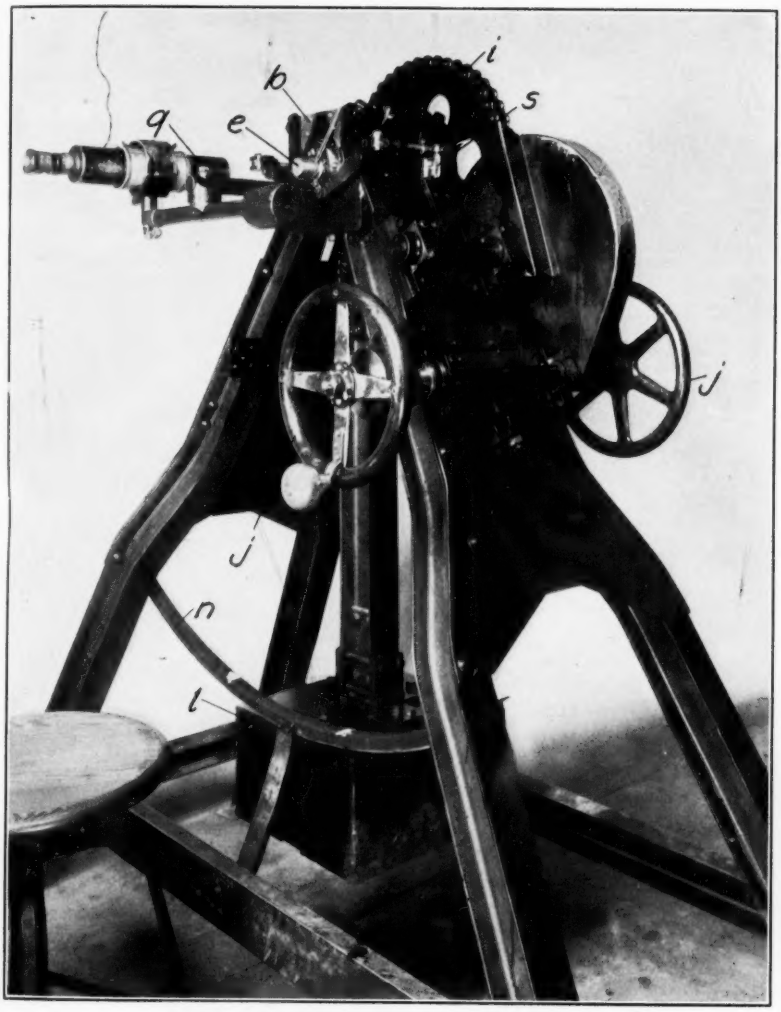

FIGURE 25.—*Torque-tension testing machine*

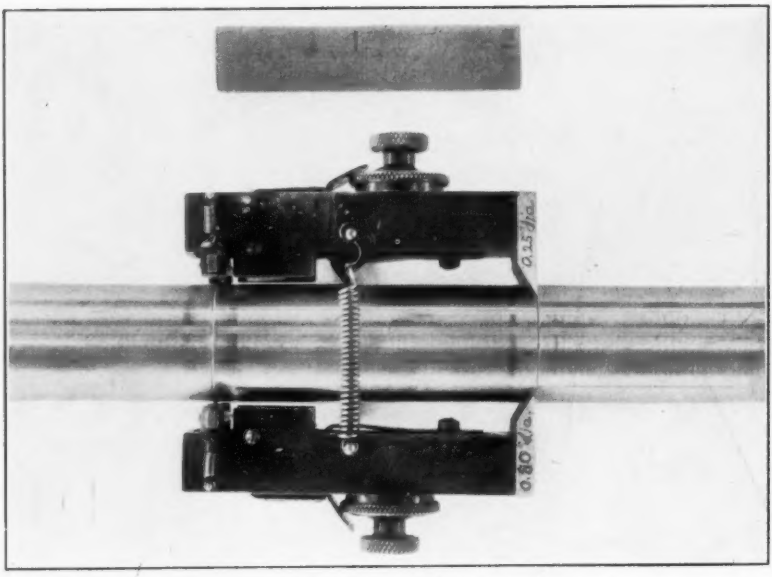

FIGURE 27.—*Tuckerman optical strain gages*

To the pendulum axle, *a*, was rigidly attached the pendulum, *l*. When the driving sprocket was rotated so as to tighten the device on the bolt, the tensile stress in the bolt, *d*, increased. This stress was measured, using two Tuckerman optical strain gages, *m*, one on each side of the shank of the bolt. The pendulum axle was cut away to allow the strain gages to be attached to the bolt.

Tightening the device on the bolt also increased the torque on the bolt and the pendulum axle. The torque caused rotation of the pendulum axle in the ball bearings, moving the pendulum from its lowest position until the torque exerted by the pendulum in one direction of rotation equaled the torque exerted by the device in the opposite direction.

A pointer on the pendulum moved over a curved scale, *n*, which was graduated to indicate the torque exerted by the pendulum. Simultaneous readings of the strain gages and of the torque scale were used to determine the relation of torque to tension for the device being tested.

In a similar way the uncrewing torque was measured, when the device was loosened, by rotating the driving sprocket in the opposite direction, permitting the pendulum to swing to its lowest position, zero on the scale, and then up on the other side of the scale.

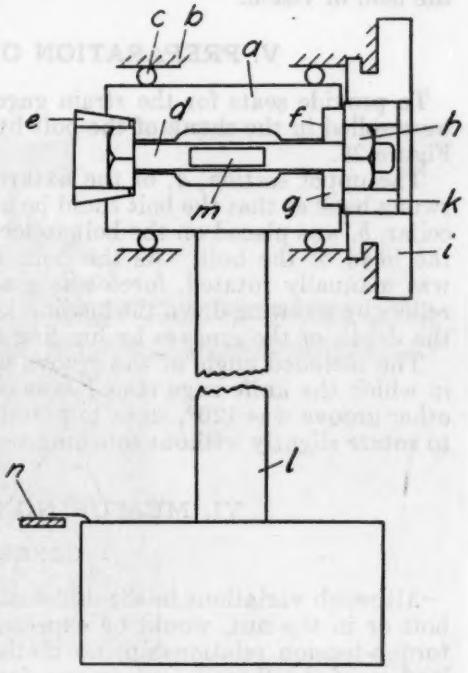

FIGURE 26.—*Torque-tension testing machine, schematic drawing*

This machine was calibrated by applying two horizontal forces to the axle of the pendulum, acting in opposite directions, to form a couple. The perpendicular distance between the forces was 40 inches. The forces were applied by dead weight to flexible steel bands passing over pulleys having ball bearings. The error in the readings of the machine did not exceed one-half of 1 per cent.

2. TUCKERMAN OPTICAL STRAIN GAGE

The Tuckerman optical strain gages,[11] having a 2-inch gage length, are shown in Figure 27, mounted on one of the bolts.

These gages are used with an autocollimator, *q*, and auxiliary prism, *s*, Figure 25. This autocollimated observing system permitted the

[11] A description of the Tuckerman optical strain gage and autocollimated observing system will be found in the Proceedings of the American Society for Testing Materials, vol. 23, 1923, Pt. II, technical papers, pp. 602-610; in Engineering, London, vol. 116, 1923, pp. 222-223; and in Paper No. 335, World Engineering Congress, Tokyo, Japan, pp. 33-36, Precision Machines and Instruments for the Measurement of Length. by George K. Burgess.

strain in the bolt to be measured within one-millionth of an inch per inch, corresponding to a stress in the body of the bolt of 29 lb. per sq. in. The two strain gages and autocollimator were calibrated with an interferometer.

As direct observation of the seating of the knife-edges and lozenges of the strain gages in the grooves in the bolt was prevented by the pendulum axle and the frame of the machine, a laryngoscope was used to observe these contact points when the strain gages were put into place. This instrument consisted of a periscope and a small electric light adjacent to the reflecting prism of the periscope for illuminating the field of vision.

V. PREPARATION OF SPECIMENS

To provide seats for the strain gages two grooves, 2 inches apart, were rolled in the shank of the bolt by means of the fixture shown in Figure 28.

The upper section, *a*, of the fixture was hinged, allowing it to be swung back so that the bolt could be placed in the fixture. A spacing collar, *b*, was placed on the bolt to locate the grooves with respect to the head of the bolt. As the bolt, supported on the rollers, *c*—*c*, was manually rotated, force was gradually applied to the grooving rollers by screwing down the loading knob, *d*. Stops, *e*—*e*, controlled the depth of the grooves by limiting the travel of the upper section.

The included angle of the groove nearest to the head of the bolt, in which the knife edge rested, was 60°. The included angle of the other groove was 120°, so as to permit the lozenge of the strain gage to rotate slightly without touching the sides of the grooves.

VI. MEASURING SPECIMENS

1. GENERAL

Although variations in the dimensions of the threads, either on the bolt or in the nut, would be expected to affect to some extent the torque-tension relationship, no method of measuring the errors in lead or of the thread contour was found which could be used on all the devices.

The methods which are used for ordinary threads could not be used for the nuts and bolts having deformed threads; therefore the devices having ordinary threads were not measured by the usual methods. Moreover, such measurements would have been tedious and expensive.

As it was believed that differences in the dimensions of the threads sufficiently great to affect the torque-tension relationships would be indicated by measuring the diametral clearance between the nut and the bolt when assembled and the obliquity of the bearing face of the nut, these measurements were made on all ordinary nuts and on all the other devices on which it was practicable. These values were used to determine whether the ordinary bolts and nuts complied with the purchase specifications.

Each bolt and device was examined visually. None of the devices submitted by the manufacturers showed any defects. A few of the ordinary nuts did not have full threads and were therefore discarded.

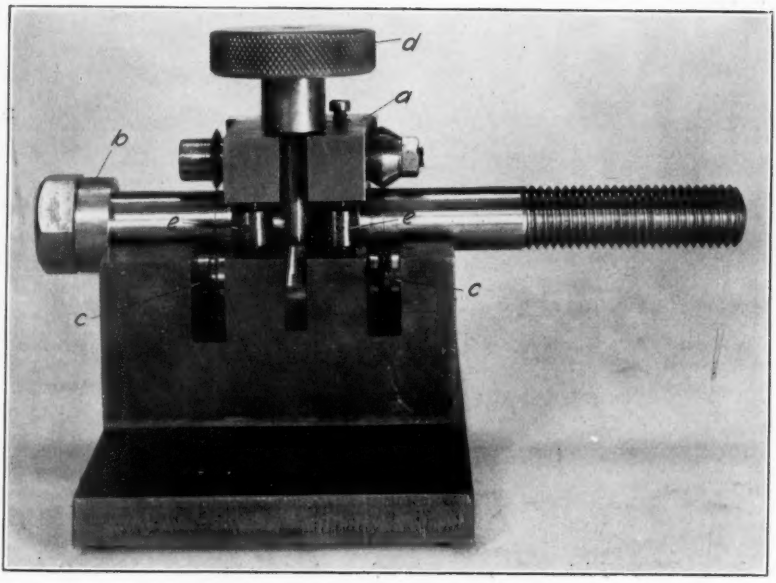

FIGURE 28.—*Fixture for grooving bolts*

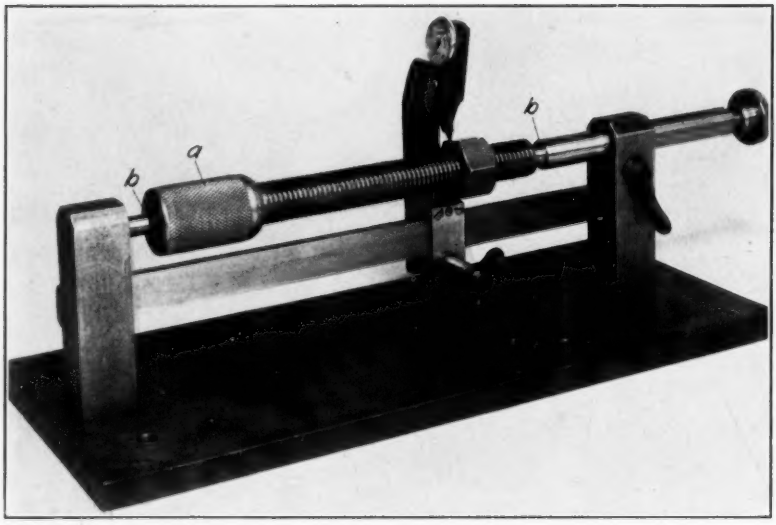

FIGURE 29.—*Fixture for measuring the obliquity of the face of the nut*

2. CLEARANCE BETWEEN THREADS OF NUT AND BOLT

The clearance between the threads in the nut and those on the bolt was measured by the fixture shown in Figure 24. The bolt was secured in the fixture by the clamping plate, *a*, and thumbscrew, *b*. The spindle of the dial micrometer rested on a corner of the nut directly over the axis of the bolt. A small upward force was applied to the nut by the fingers while the nut was rotated back and forth through a small angle, and the maximum reading recorded. This operation was repeated with a small downward force applied to the nut. The difference between these two readings was taken as the diametral clearance between the nut and bolt. The results are given in Table 4.

TABLE 4.—*Diametral clearance between threads of nut and bolt*

Device	Maximum	Minimum	Average
	Inch	*Inch*	*Inch*
I. American National coarse-thread regular nut	0.0082	0.0058	0.0073
II. U. S. standard regular nut	.0079	.0060	.0069
III. American National fine-thread regular nut	.0016	.0010	.0014
IV. American National coarse-thread regular nut and a jam nut	.0082	.0058	.0073
V. U. S. standard regular nut and a jam nut	.0079	.0060	.0069
VI. American National fine-thread regular nut and a jam nut	.0016	.0010	.0014
VII. U. S. standard slotted nut and a cotter pin	.0079	.0060	.0069
VIII. American National fine-thread castellated nut and a cotter pin	.0016	.0010	.0014
A	.0091	.0033	.0070
B	.0018	.0008	.0012
B-U. S	.0010	.0000	.0006
C	.0066	.0038	.0050
D, deformed nut			
E	.0088	.0030	.0068
F	.0098	.0050	.0074
G	.0088	.0040	.0057
H	.0101	.0059	.0076
I	.0062	.0040	.0051
J	.0074	.0036	.0055
K	.0100	.0039	.0049
L, pin prevented measurement			
M	.0100	.0048	.0071
N	.0149	.0027	.0066
O	.0086	.0033	.0055
P	.0081	.0017	.0060
Q	.0051	.0016	.0036
R	.0081	.0049	.0068
S	.0080	.0024	.0051
T	.0059	.0018	.0040
U	.0072	.0000	.0027
V, deformed thread			
AA to JJ, spring washers	.0079	.0060	.0069

3. OBLIQUITY OF FACE OF NUT

The obliquity of the bearing faces of the nuts was measured, using the fixture shown in Figure 29. Nuts having deformed threads and those having certain locking features which interfered with the bolt threads could not be measured, as they could not be screwed on the mandrel.

The mandrel was mounted between the centers, *b*—*b*, and the dial micrometer adjusted to bring the spindle into contact with the bearing face of the nut, $^{17}/_{32}$ inch from center. The mandrel was then rotated, and the maximum and minimum readings of the dial recorded. The difference between these readings was taken as a measure of the obliquity of the bearing face. If the difference was zero, the bearing face was perpendicular to the axis of the nut. The values for each device are given in Table 5.

TABLE 5.—*Obliquities of face of nuts*

Device	Obliquities		
	Maximum	Minimum	Average
	Inch	*Inch*	*Inch*
I. American National coarse-thread regular nut	0.014	0.003	0.009
II. U. S. standard regular nut	.010	.003	.006
III. American National fine-thread regular nut	.030	.003	.010
IV. American National coarse-thread regular nut and a jam nut	.016	.002	.009
V. U. S. standard regular nut and a jam nut	.012	.001	.005
VI. American National fine-thread regular nut and a jam nut	.009	.001	.006
VII. U. S. standard slotted nut and a cotter pin	.010	.002	.004
VIII. American National fine-thread castellated nut and a cotter pin	.009	.000	.005
A	.015	.008	.011
B	.006	.000	.003
B–U. S.	.007	.002	.005
C, cast face; does not bear			
D, unfinished nut	.028	.011	.020
E	.008	.003	.005
F	.005	.002	.003
G	.016	.002	.007
H	.030	.004	.011
I	.011	.005	.007
J, cast nut, face V shaped			
K	.013	.001	.005
L	.029	.008	.017
M	.015	.009	.012
N, face does not bear			
O, face beveled			
P, face V shaped			
Q	.014	.002	.009
R	.006	.001	.003
S	.019	.004	.008
T, face does not bear			
U	.010	.003	.006
V	.012	.005	.008
AA to JJ	.010	.003	.006

VII. METHOD OF TEST

1. TORQUE-TENSION

Because of differences in the construction and behavior of the different devices it was found impossible to follow exactly the same test procedure for all.

In the simplest procedure five specimens were used. Three specimens were tested as follows: Each specimen was placed in the torque-tension machine and the nut screwed on until the stress in the bolt was about 5,000 lb. per sq. in. The stress and the screwing-on torque were recorded, as at *a*, Figure 30, which is a typical torque-tension graph drawn to assist the reader in understanding the method of testing.

The nut was then screwed off slightly and the initial screwing-off torque at that stress in the bolt was recorded, as at *b*. The nut was then further screwed on until the stress in the bolt was about 7,000 lb. per sq. in., as at *c*, and screwed off slightly to obtain the initial screwing-off torque for that stress, as at *d*. The stresses were successively increased to obtain the values at *e*, *f*, etc., up to about 20,000 lb. per sq. in. in the body of the bolt.

To determine the relation between the stress in the bolt and the continuous screwing-off torque as the stress was decreased from 10,000 lb. per sq. in. to zero and from 20,000 lb. per sq. in. to zero, two specimens were tested. With one of these specimens the nut was screwed

on, without backing off at intermediate stresses, until the stress in the bolt was about 10,000 lb. per sq. in. as at *g*, Figure 30, then screwed off to obtain the values of continuous screwing-off torque, *h*, *i*, *j*, and zero. The other specimen was screwed on to about 20,000 lb. per sq. in. as at *o*, then the nut was screwed off to obtain the values *p*, *q*, *r*, *s*, *t*, and zero. For many of the devices this simple procedure was not feasible. For these it was found that the slight unscrewing of the device necessary to determine the initial screwing-off torque altered the bearing surfaces enough to make further values of the screwing-on torque significantly different from the values obtained by continuous screwing on. For these devices nine specimens were tested. For three speci-

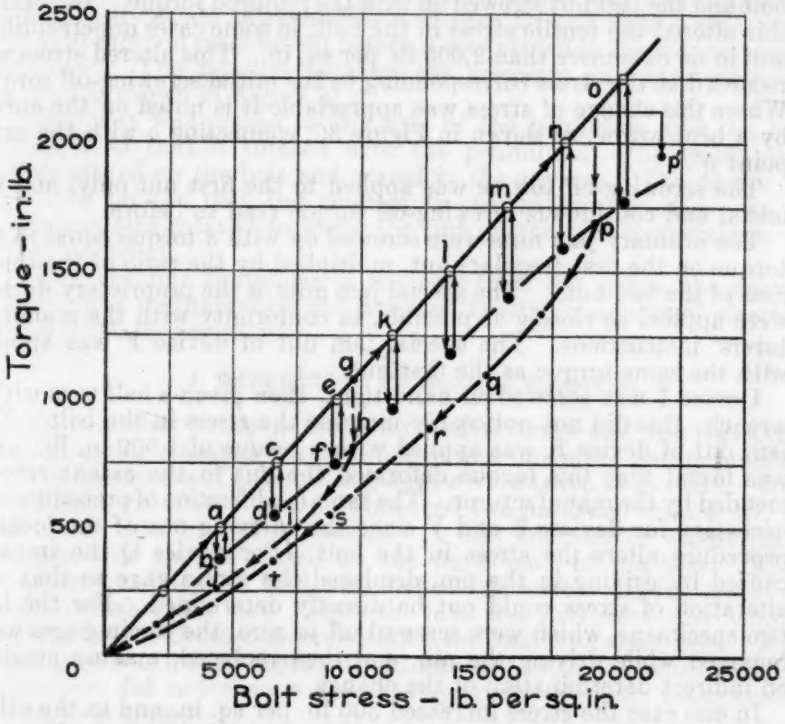

FIGURE 30.—*Typical torque-tension graph to illustrate method of testing*

mens the nut was screwed on, without backing off, until the stress in the bolt was about 10,000 lb. per sq. in. and the values *a*, *c*, *e*, and *g*, Figure 30, obtained. The nut was then screwed off to obtain the values of *h*, *i*, *j*, and zero. In the same way three specimens were tested stressing the bolt to about 15,000 lb. per sq. in. and three stressing the bolt to about 20,000 lb. per sq. in. For specimens stressed to 20,000 lb. per sq. in., the values as shown by Figure 30 are *a*, *c*, *e*, *k*, *l*, *m*, *n*, and *o* for the screwing-on torques, and *p*, *q*, *r*, *s*, *t*, and zero for the screwing-off torques. Three devices, H, Q, and II, were tested before this procedure was standardized. For these, 11 specimens were tested. For H continuous screwing-off curves at 1,500 in. lbs. torque were not made on two specimens but were later made on two additional specimens. Even with this larger number of

specimens it was possible to determine the initial screwing-off torque at only three different stresses. There seemed to be no need for increasing this number further. For Q and II screwing-on and initial screwing-off torques were measured on nine specimens. For the other two, continuous screwing-off torques were determined.

Where the locking device used two nuts, a further change in the test procedure became necessary. Nine specimens were tested as before, with the following modification. The first nut was screwed on, reading the values of the screwing-on torque and stress as *a*, *c*, *e*, *g*, Figure 30, until the desired stress (10,000, 15,000, or 20,000 lb. per sq. in.) was reached. The first nut was then held so that it did not turn on the bolt and the jam nut screwed on with the required torque. In general, this altered the tensile stress in the bolt, in some cases imperceptibly, and in no case more than 2,000 lb. per sq. in. This altered stress was recorded as the stress corresponding to the initial screwing-off torque. Where this change of stress was appreciable it is noted on the curves by a bent arrow, as shown in Figure 30, connecting *o* with the extra point *p'*.

The screwing-off torque was applied to the first nut only, and the initial and continuous screwing-off torque read as before.

The ordinary jam nuts were screwed on with a torque equal to the torque on the first (regular) nut, multiplied by the ratio of the thickness of the two nuts. The special jam nuts of the proprietary devices were applied as closely as possible, in conformity with the manufacturers' instructions. The special jam nut of device F was applied with the same torque as the first nut.

Device I was screwed on hand-tight, then given a half turn with a wrench; this did not noticeably increase the stress in the bolt. The jam nut of device K was applied with a torque of 1,000 in. lb., as it was found that this torque deformed the nut to the extent recommended by the manufacturer. The same modification of procedure was necessary for devices S and V since the carrying out of the locking procedure alters the stress in the bolt. For device Q the impact, caused by driving in the pin, displaced the strain gage so that the alteration of stress could not be directly determined. For the last two specimens, which were screwed off to zero, the strain gages were removed while driving the pin, and then replaced, making possible an indirect determination of the change.

In one case the stress increased 300 lb. per sq. in. and in the other case decreased 2,000 lb. per sq. in. The initial screwing-off curves are therefore plotted as if there had been no change in stress. For all jam nuts (*IV*, *V*, *VI*, F, I, and K) and for devices Q and S, the screwing-on torques recorded are the same as if no locking device had been used. The locking device affects only the screwing-off torques.

In plotting all of these torque-tension curves large open circles were used for screwing-on torques and large solid circles for the initial screwing-off torques. For the continuous screwing-off torques small solid circles were used.

A new bolt was used for each specimen, also a new regular nut, if one was used with the device. The face of the bearing washer was reground for each test, using a cylindrical grinder and a fine feed. The grinder marks were circular about the axis of the bolt, and the faces were smooth, flat and parallel.

When the spring washers were tested, it was found that the continuous screwing-off torque fluctuated considerably, caused probably, by the ends of the spring washers cutting into the bearing washer and into the nut, then releasing suddenly. This, however, did not prevent the use of the simplest test procedure except in the case of device II.

For device II these fluctuations in the torque displaced the strain gages making it impossible to obtain satisfactory readings of the stress in the bolt when the nut was unscrewed. Consequently, the second procedure with 11 specimens was used for this device.

Each locking device, bolt, and bearing washer was first thoroughly cleaned in carbon tetrachloride and then flushed with a good grade of light mineral machine oil before it was placed in the torque-tension machine. The relation between the viscosity and temperature of the oil is shown in Figure 31.

The bolt was placed in the axle of the pendulum and the head wedged so that it rotated with the pendulum. The strain gages were placed on the bolt and seated in the grooves. The device was screwed on the bolt and coupled to the driving sprocket. As the sprocket was rotated to screw the nut on the bolt the strain in the bolt increased.

To determine the stress in the bolt from the strain, the average strain was multiplied by the average Young's modulus of elasticity 28,900,000 lb. per sq. in.

2. DEFLECTION OF SPRING WASHERS

The relation between the compressive forces and the deflections of the spring washers was determined in a universal testing machine. Three specimens of each locking device were taken at random. Each specimen was placed on a bolt between two hardened collars, and the bolt was then loaded in tension. A dial micrometer was adjusted so that the spindle rested on the upper end of the bolt. Simultaneous readings of load and deflection were recorded until the spring washer was flat. Then the load was decreased and readings of load and deflection recorded until the load was again zero. Each specimen was loaded repeatedly in this way until the behavior of the specimen did not change appreciably, many of them being loaded five or six times.

VIII. RESULTS

The results obtained in the torque-tension machine are shown graphically in Figures 32 to 72, inclusive. The number of specimens tested (5, 9, or 11) indicates the particular test procedure used. The coordinates of each point on these graphs are the averages of the stress and torque values obtained on all specimens tested in the same way. The stresses are in all cases the averages of the tensile stresses in the bodies of the bolts. To obtain the stress in the bolt at the root of the American National coarse and U. S. standard thread or at the pitch line of the thread, the stresses given must be multiplied by 1.46 and 1.20, respectively. The stresses shown for the American National fine thread, Figures 34, 37, and 39, must be multiplied by 1.12 and 1.06 to find the stresses at the root and at the pitch line of the threads, respectively.

The screwing-on and initial screwing-off torques for stresses of 5,000, 10,000, 15,000, and 20,000 lb. per sq. in. in the bolt, read from the curves, are given in Table 6. The ratios of the screwing-off torque for each device to the screwing-off torque for the American National coarse-thread nut at stresses of 10,000, 15,000, and 20,000 lb. per sq. in. are also given.

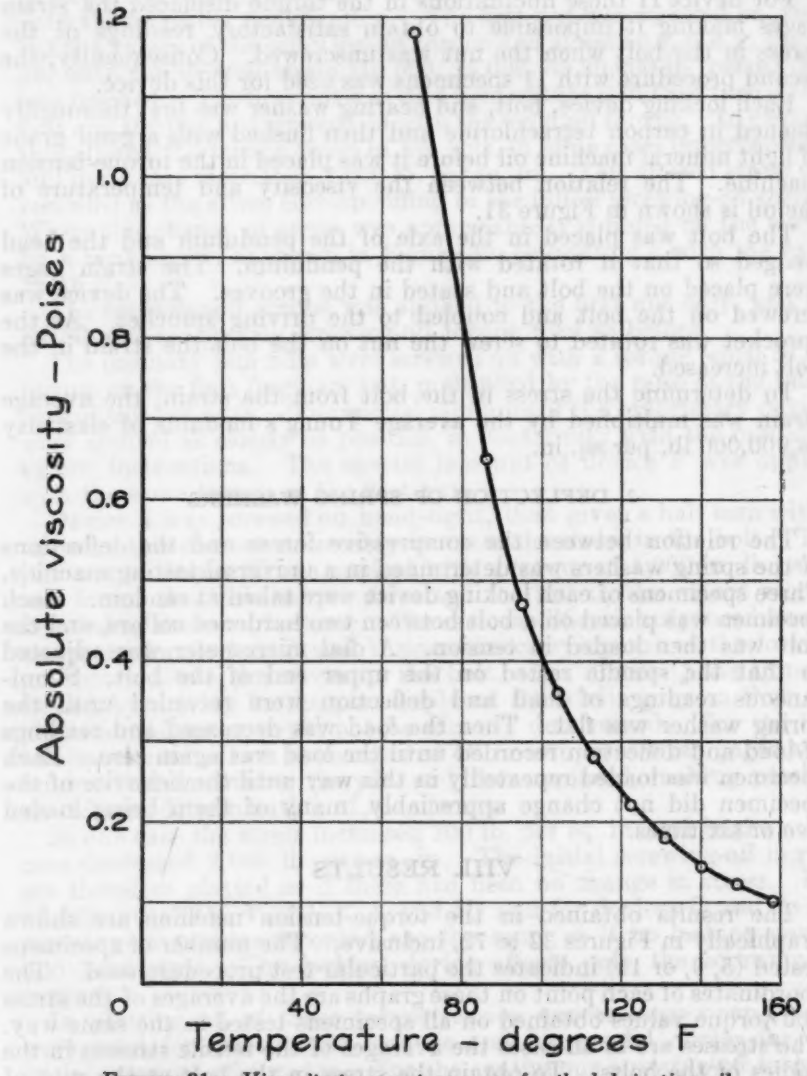

FIGURE 31.—*Viscosity-temperature curve for the lubricating oil*

These ratios were plotted, arranging them in numerical order, beginning with the lowest value. The ratios for stresses of 10,000 lb. per sq. in. are shown in Figure 77, those for 15,000 lb. per sq. in. in Figure 78, and for 20,000 lb. per sq. in. in Figure 79.

TABLE 6.—*Values of torque and stress*

Symbol of device	Figure No.	Stress, 5,000 lb. per sq. in.		Stress, 10,000 lb. per sq. in.			Stress, 15,000 lb. per sq. in.			Stress, 20,000 lb. per sq. in.		
		Torque, inch-pounds		Torque, inch-pounds		Ratio to American National coarse initial screwing off	Torque, inch-pounds		Ratio to American National coarse initial screwing off	Torque, inch-pounds		Ratio to American National coarse initial screwing off
		Screwing on	Initial screwing off	Screwing on	Initial screwing off		Screwing on	Initial screwing off		Screwing on	Initial screwing off	
I	32	420	-------	840	690	1.00	1,260	1,060	1.00	1,680	1,440	1.00
II	33	410	-------	830	750	1.09	1,250	1,100	1.04	1,660	1,450	1.01
III	34	350	-------	690	600	.87	1,030	920	.87	1,370	1,200	.83
IV	35	420	-------	800	820	1.19	1,210	1,080	1.02	1,590	1,340	.93
V	36	440	-------	870	660	.96	1,310	1,100	1.04	1,750	1,550	1.13
VI	37	390	-------	750	640	.93	1,100	980	.92	1,460	1,310	.08
VII	38	440	-------	820	750	1.09	1,200	1,140	1.08	1,580	1,480	1.90
VIII	39	410	-------	750	780	1.13	1,070	1,050	.99	1,410	1,320	.92
A	40	560	-------	980	850	1.23	1,400	1,220	1.15	1,820	1,600	1.11
B	41	1,050	1,020	1,950	1,800	2.61	2,260	2,020	1.91	2,580	2,230	1.55
B–US	42	940	870	1,780	1,700	2.46	2,290	2,100	1.98	2,610	2,350	1.63
C	43	570	480	1,290	1,100	1.59	2,560	2,040	1.92	2,910	2,450	1.70
D	44	1,040	960	1,400	1,270	1.84	1,760	1,580	1.49	2,120	1,900	1.32
E	45	440	-------	840	710	1.03	1,250	1,040	.98	1,650	1,360	.94
F	46	450	-------	870	1,010	1.46	1,280	1,780	1.68	1,700	2,550	1.77
G	47	430	-------	820	720	1.04	1,200	1,030	.97	1,590	1,300	.90
H	48	375	-------	740	510	.74	1,110	910	.86	1,480	1,270	.88
I	49	430	-------	870	750	1.09	1,300	1,140	1.08	1,750	1,550	1.08
J	50	460	390	820	680	.99	1,190	1,010	.95	1,710	1,430	.99
K	51	420	-------	850	760	1.10	1,270	1,170	1.10	1,690	1,570	1.09
L	52	470	-------	830	700	1.01	1,170	1,030	.97	1,510	1,360	.94
M	53	580	-------	1,020	650	.94	1,420	980	.92	1,800	1,310	.91
N	54	400	-------	800	500	.72	1,340	900	.85	1,900	1,290	.90
O	55	460	360	830	630	.91	1,190	870	.82	1,490	1,080	.75
P	56	410	350	770	620	.90	1,130	900	.85	1,480	1,180	.82
Q	57	510	-------	990	870	1.26	1,470	1,360	1.28	1,950	1,840	1.28
R	58	500	430	900	830	1.20	1,310	1,220	1.15	1,720	1,620	1.12
S	59	450	-------	860	800	1.16	1,270	1,100	1.04	1,690	1,400	.97
T	60	560	850	1,000	850	1.23	1,430	1,110	1.05	1,880	1,420	.99
U	61	470	-------	880	690	1.00	1,300	1,130	1.07	1,710	1,560	1.08
V	62	510	-------	880	760	1.10	1,200	980	.92	1,500	1,200	.83
AA	63	440	340	800	630	.91	1,140	920	.87	1,480	1,200	.83
BB	64	450	340	780	590	.86	1,100	850	.80	1,420	1,100	.76
CC	65	540	640	960	730	1.06	1,380	1,040	.98	1,800	1,430	.99
DD	66	480	520	900	650	.94	1,280	950	.90	1,640	1,260	.88
EE	67	470	420	850	740	1.07	1,220	1,020	.96	1,590	1,320	.92
FF	68	510	440	940	840	1.22	1,380	1,210	1.14	1,810	1,600	1.11
GG	69	430	360	760	630	.91	1,070	900	.85	1,380	1,180	.82
HH	70	500	350	860	570	.83	1,190	830	.78	1,510	1,110	.77
II	71	610	-------	1,000	750	1.09	1,370	980	.92	1,690	1,210	.84
JJ	72	500	380	840	600	.87	1,170	800	.75	1,500	1,100	.76

The results of the deflection tests of spring washers are shown graphically in Figure 73.

The appearance of the nuts and bearing washers after the tests of the spring washers is shown in Figures 74, 75, and 76.

IX. DISCUSSION

1. GENERAL

To aid in interpreting these results it was thought desirable to form some estimate of deviations of the test results for nominally identical specimens. For this purpose a thorough study was made of the data for the regular nuts.

In screwing on, devices *I* and *IV* (regular American National coarse-thread nuts) were like devices under like test conditions. Similarly

in screwing on, devices *II*, *V*, I, K, and S (regular U. S. standard nuts) were alike. Device *VII* was from different stock, but differed from these nominally only in the slot for the cotter pin. Also, in screwing on, devices *III* and *VI* were alike. Device *VIII* was from different stock, but differed from these nominally only in the castellated top. Within each of these groups the deviation of the screwing-on torque of the individual device from the mean is a measure of the variation in the behavior of nominally identical devices.

The maximum deviation from the mean of the screwing-on torques in any one of these groups for stresses above 10,000 lb. per sq. in. is 6.1 per cent. Differences of less than 6 per cent between screwing-on torques for different devices are therefore probably of no significance.

No such large group of like specimens was available for a study of initial screwing-off torques. The detailed study was confined to devices *I*, *II*, and *III*. Between individual specimens the maximum deviations from the mean which were found, expressed as percentages of the screwing-on torque, were:

	Per cent
Screwing-on torque	6
Initial screwing-off torque	6
Difference between screwing-on and screwing-off torques	5

The differences between individual specimens of the other devices were in most cases considerably greater than for the regular nuts. Consequently, differences of less than 6 per cent, or even more, in these quantities are probably of no significance. It is to be noted that if the screwing-on and the screwing-off torques on the same nut and bolt were independent the differences should be expected to show larger deviations, approaching 9 per cent in value.

2. PERSY'S THEORY

Omitting negligible second-order terms, Persy's theoretical discussion applied to ⅞-inch regular nuts leads to the following relations:

American National coarse and U. S. standard thread screwing-on torque

$$\frac{T}{S}=0.442\,Rf'+0.175\,f+0.00703$$

Screwing-off torque

$$\frac{t}{S}=0.442\,Rf'+0.175\,f-0.00703$$

$$\text{Difference } \frac{(T-t)}{S}=0.0141$$

American National fine-thread screwing-on torque

$$\frac{T}{S}=0.442\,Rf'+0.181\,f+0.00439$$

Screwing-off torque

$$\frac{t}{S}+0.442\,Rf'+0.181\,f-0.00439$$

$$\text{Difference } \frac{(T-t)}{S}=0.00879$$

where T = screwing-on torque (in. lb.).
t = screwing-off torque (in. lb.).
S = stress in bolt (lb. per sq. in.).
R = effective bearing radius of nut on washer (in.).
f' = coefficient of friction of nut on washer.
f = coefficient of friction of nut threads on bolt threads.

In these expressions three quantities, R, f', and f, occur, which are known to vary considerably with small changes in the bearing surfaces, such as smoothness of finish, lubrication, etc.

In view of the variations found in the experiments between nominally identical devices, no close check of these formulæ could be expected. They can, however, serve in some cases to give a general idea of the behavior of regular nuts and bolts.

3. CLEARANCES AND OBLIQUITY OF BEARING FACE OF NUT

Detailed studies were made of the individual test results from regular nuts. The scatter diagrams plotted showed a wholly random distribution. Within the limits used in these tests, neither clearance of nut on bolt nor obliquity of the bearing face of the nut measurably affected the torques.

4. DEVICES

Devices *I*, *II*, and *III*. Regular nuts

From Persy's theory we should conclude that for these devices the screwing-on torque should be proportional to the stress, that the initial screwing-off torque and the continuous screwing-off torque should be the same and proportional to the stress. If the coefficients of friction remained constant, the difference between the screwing-on and screwing-off torques should be the same for *I* and *II*, smaller for *III*, and be calculable from the equations. If, in addition, the coefficients of friction were the same in all three devices we should expect the screwing-on torques for *I* and *II* to be nearly identical and greater than for *III*.

The curves show that, with accidental variations found in the behavior of devices, these conclusions are fairly well borne out. The screwing-on curves are straight lines through the origin. The initial screwing-off and continous screwing-off curves show greater discrepancies, which may be due to changes in the coefficients of friction. The fact that the continuous screwing-off curves for device *I* lie somewhat above the initial screwing-off curve, for device *II* almost coincide with it, and for device *III* lie somewhat below, can not be caused by any differences in the design of the three devices, but are probably caused by differences in the small changes in the condition of the bearing surfaces during the test.

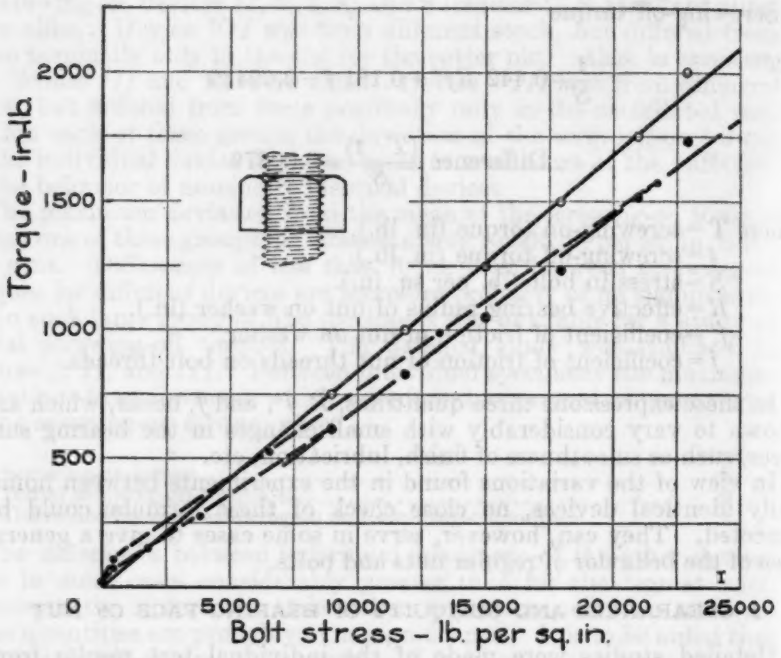

FIGURE 32.—*Torque-tension curves for device I. American National coarse-thread regular nut. Five specimens were tested*

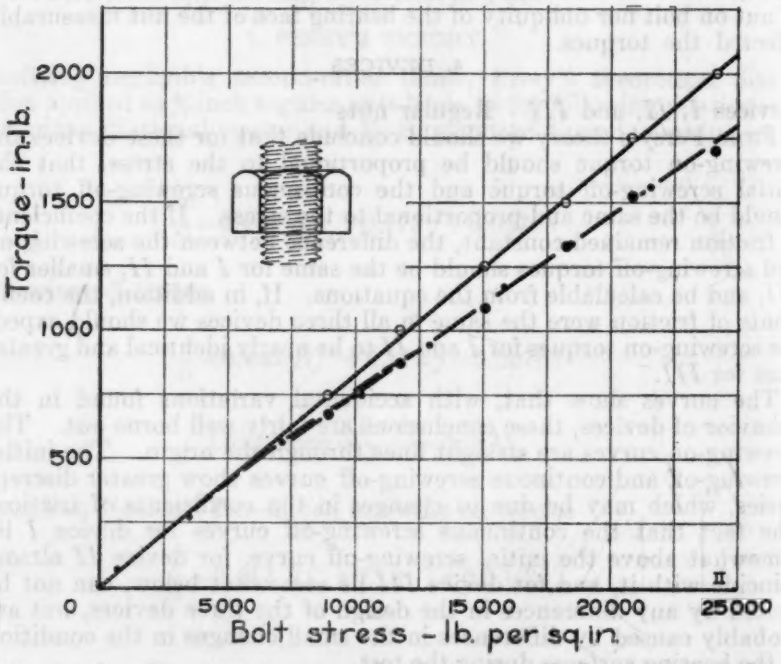

FIGURE 33.—*Torque-tension curves for device II. U. S. standard regular nut. Five specimens were tested*

A comparison of the differences between the screwing-on and initial screwing-off stresses is given in Table 7.

TABLE 7.—*Ratio of difference between screwing-on and initial screwing-off torques to stress in bolt*

Device	$\frac{T-t}{S}$				Number of readings	
	Theoretical	Observed			Larger than theoretical value	Total
		Min.	Max.	Aver.		
	*In.*³	*In.*³	*In.*³	*In.*³		
I. American National coarse-thread regular nut	0.0141	0.0094	0.0188	0.0132	6	18
II. U. S. standard regular nut	.0141	.0066	.0152	.0098	3	17
III. American National fine-thread regular nut	.0088	.0053	.0112	.0079	3	14

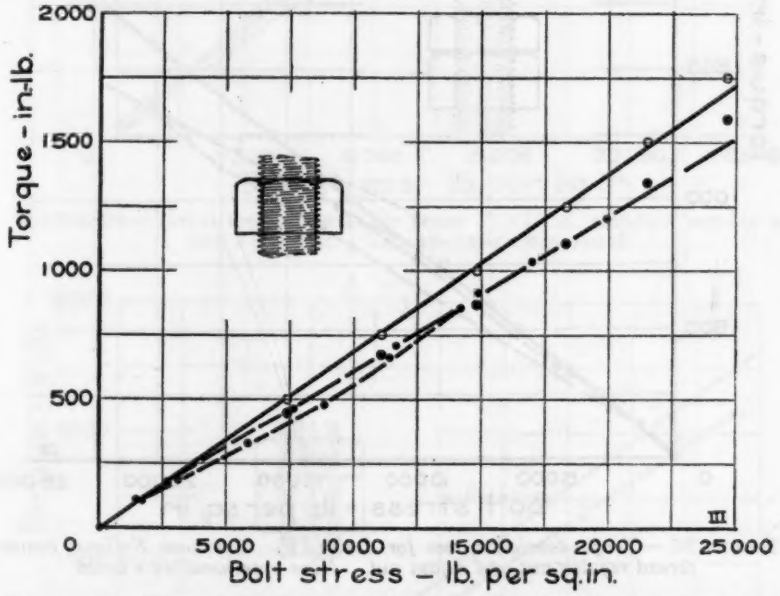

FIGURE 34.—*Torque-tension curves for device III. American National fine-thread regular nut. Five specimens were tested*

The average in each case lies considerably below the theoretical value, and the scatter of the observations is large. This seems to indicate definitely a change of the condition of the bearing surfaces during the test.

The screwing-on torques for devices *I* and *II* are considerably higher than those calculated from the table given by Case.[12] Case gives 0.15 as the coefficient of friction "when a reasonably well-lubricated bolt is tightened." Other authors, without specifying the conditions of lubrications, give torques corresponding to coefficients of friction ranging in different cases from 0.074 to 0.21.

[12] Loc. cit., p. 930.

On the assumption that $f=f'$; that is, that the coefficient of friction between nut and bolt is the same as between nut and washer, the average value of f was calculated by Persy's theory from the screwing-on torques at 20,000 lbs. per sq. in. stress. The values were: For device *I*, $f=0.20$; for device *II*, $f=0.19$; and for device *III*, $f=0.17$.

Devices *IV*, *V*, and *VI*. Regular nuts with jam nuts.

The screwing-on torques for these devices are, within the variations previously discussed, the same as for the regular nuts *I*, *II*, and *III*. The initial screwing-off torques and continuous screwing-off torques show differences larger in magnitude but of the same character as found in *I*, *II*, and *III*. Thus the curves for continuous screwing off

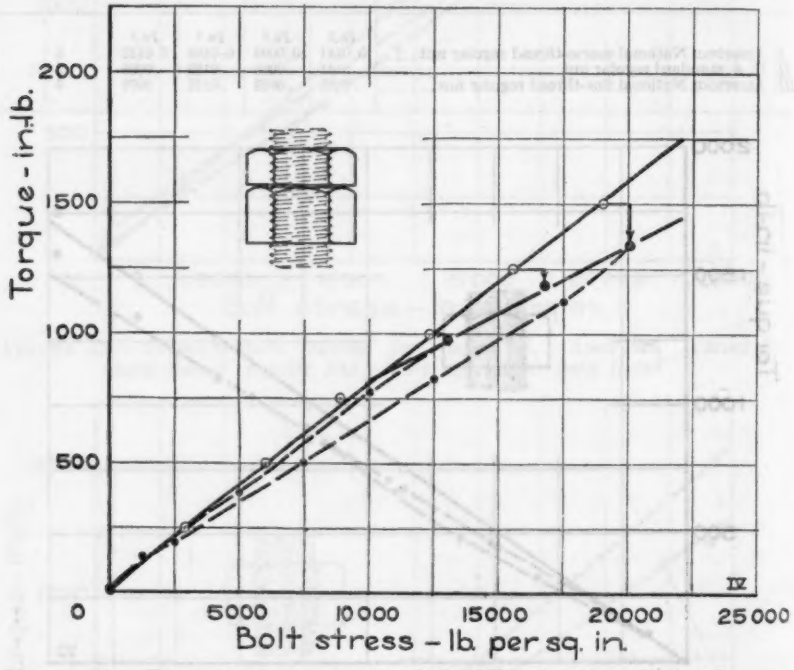

FIGURE 35.—*Torque-tension curves for device IV. American National coarse-thread regular nut and a jam nut. Nine specimens were tested*

for device *V* lies considerably above the initial screwing-off curve, for device *VI* it almost coincides with it, and for device *IV* it lies considerably below it. The differences between the screwing-on and screwing-off torques, although less uniform, average practically the same as for the regular nuts *I*, *II*, and *III*. There was, however, for the jam nuts, a small but definite final screwing-off torque at zero stress which was not present with the regular nuts alone.

Device *VII*. U. S. standard slotted nut and a cotter pin (fig. 38).

The curve for the screwing-on torques is approximately a stright line, but the deviation of the individual points from the straight line is greater than for any of the preceding devices. In addition, the average straight line prolonged cuts the axis of zero stress at about 100 inch-pounds torque.

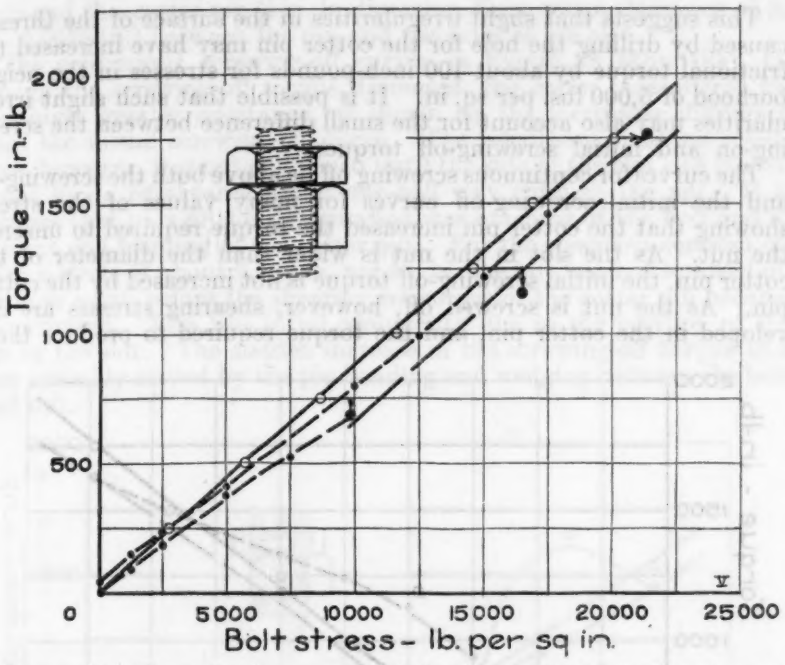

FIGURE 36.—*Torque-tension curves for device V. U. S. standard regular nut and a jam nut. Nine specimens were tested*

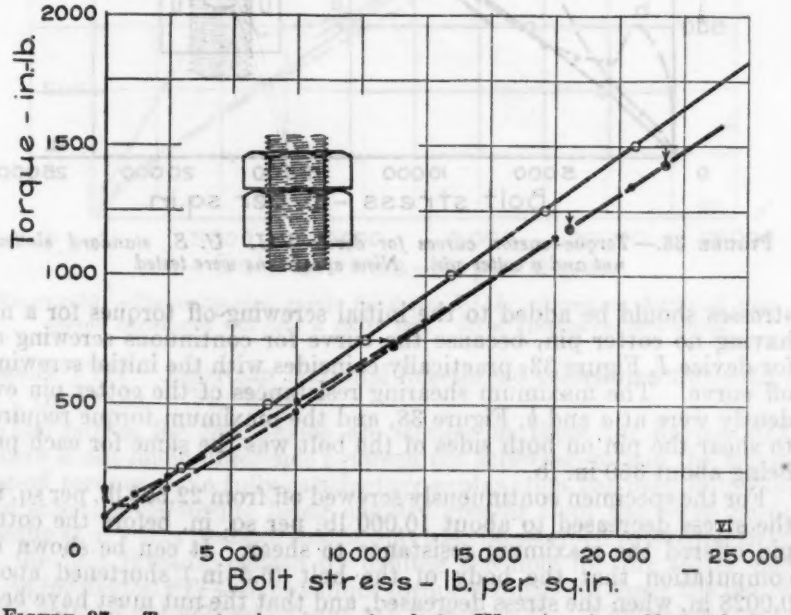

FIGURE 37.—*Torque-tension curves for device VI. American National fine-thread regular nut and a jam nut. Nine specimens were tested*

This suggests that slight irregularities in the surface of the threads caused by drilling the hole for the cotter pin may have increased the frictional torque by about 100 inch-pounds for stresses in the neighborhood of 5,000 lbs. per sq. in. It is possible that such slight irregularities may also account for the small difference between the screwing-on and initial screwing-off torques.

The curves for continuous screwing off lie above both the screwing-on and the initial screwing-off curves for many values of the stress, showing that the cotter pin increased the torque required to unscrew the nut. As the slot in the nut is wider than the diameter of the cotter pin, the initial screwing-off torque is not increased by the cotter pin. As the nut is screwed off, however, shearing stresses are developed in the cotter pin, and the torque required to produce these

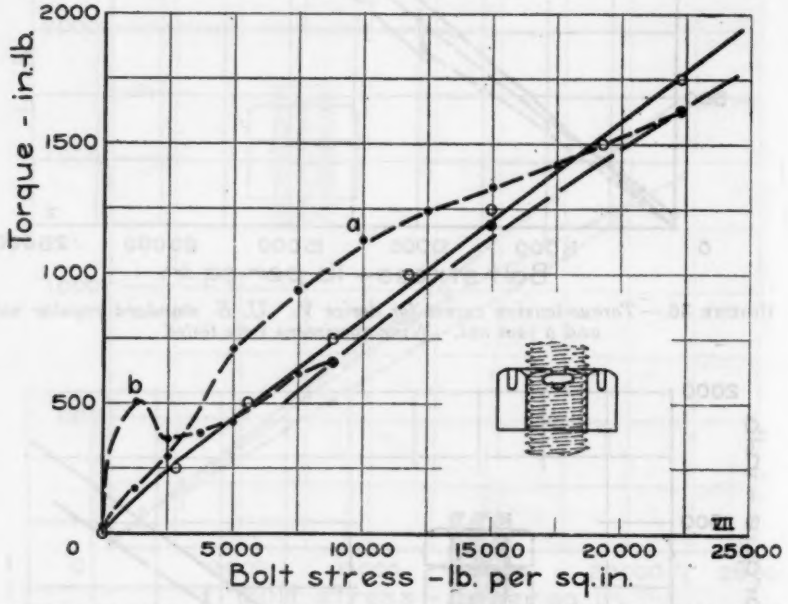

FIGURE 38.—*Torque-tension curves for device VII. U. S. standard slotted nut and a cotter pin. Nine specimens were tested*

stresses should be added to the initial screwing-off torques for a nut having no cotter pin, because the curve for continuous screwing off for device *I*, Figure 33, practically coincides with the initial screwing-off curve. The maximum shearing resistances of the cotter pin evidently were at *a* and *b*, Figure 38, and the maximum torque required to shear the pin on both sides of the bolt was the same for each pin, being about 350 in. lb.

For the specimen continuously screwed off from 22,500 lb. per sq. in. the stress decreased to about 10,000 lb. per sq. in. before the cotter pin offered the maximum resistance to shear. It can be shown by computation that the body of the bolt (6.5 in.) shortened about 0.0028 in. when the stress decreased, and that the nut must have been rotated about 0.028 turn. The side of the slot at the major diameter of the thread must have moved about 0.07 in. As the slot was $\frac{3}{16}$ in.

wide and the cotter pin ⅛ in. in diameter, there was a clearance of 1/16 in. (0.0625 in.) between the pin and the sides of the slot.

The continuous screwing-off curves in Figure 38 show that, although the screwing-off torque decreased, the cotter pins offered increasingly greater resistance, as shown by the increasing difference from the initial screwing-off curve. The maximum shearing resistance, however, was not developed until the side of the slot had moved about 1/16 in. or sheared about one-half way through the pin. It is obvious that part of this deformation was crushing of the bolt and of the nut and bending of the cotter pin. For the specimen screwed off from a stress of about 9,000 lb. per sq. in. the nut was not screwed off quite so much before the shearing resistance of the cotter pin became a maximum. This was in all probability due to the position of the pin in the slot. The sudden increase in the screwing-off torque at *b* was probably caused by the pin bending and wedging between the bolt and nut.

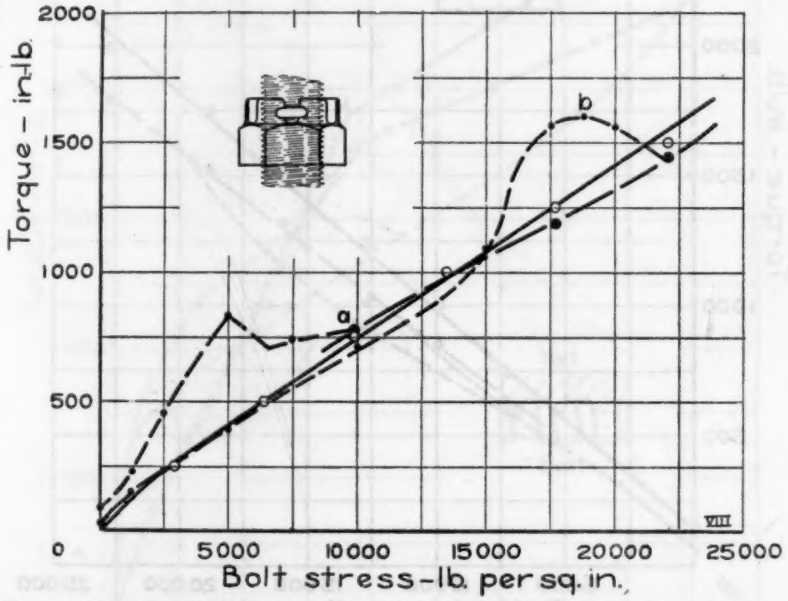

FIGURE 39.—*Torque-tension curves for device VIII. American National fine-thread castellated nut and a cotter pin. Nine specimens were tested*

Device *VIII*. American National fine-thread castellated nut with a cotter pin. (Fig. 39.)

The curves for this device are similar to those for device *VII*. There is not much difference between the screwing-on and the screwing-off torques. No fully satisfactory explanation has been found for the screwing-off torque being slightly greater than the screwing-on torque at *a*. It is possible that it may also be ascribed to irregularities in the bolt threads, caused by drilling the hole for the cotter pin.

As for device *VII* the maximum torque required to shear the pin on both sides of the bolt was about 350 inch-pounds. This value should be the same because the cotter pins for both devices had a diameter of ⅛ inch.

The curves for continuous screwing off, unlike those for device *VII*, rise rapidly from the initial value because the slots in the nuts were only $\frac{3}{32}$ inch wide and the clearance between pin and slot only $\frac{1}{32}$ inch instead of $\frac{1}{16}$ inch. The maximum shearing resistance of the pins was, therefore, developed when the side of the nut had moved only about 0.02 inch or about one-third of the movement for device *VII*.

The curves show that for the specimen continuously screwed off from about 22,500 lb. per sq. in. the cotter pin was sheared through when the stress was about 15,000 lb. per sq. in. and that the curve then followed closely the initial screwing-off curve. The maximum value

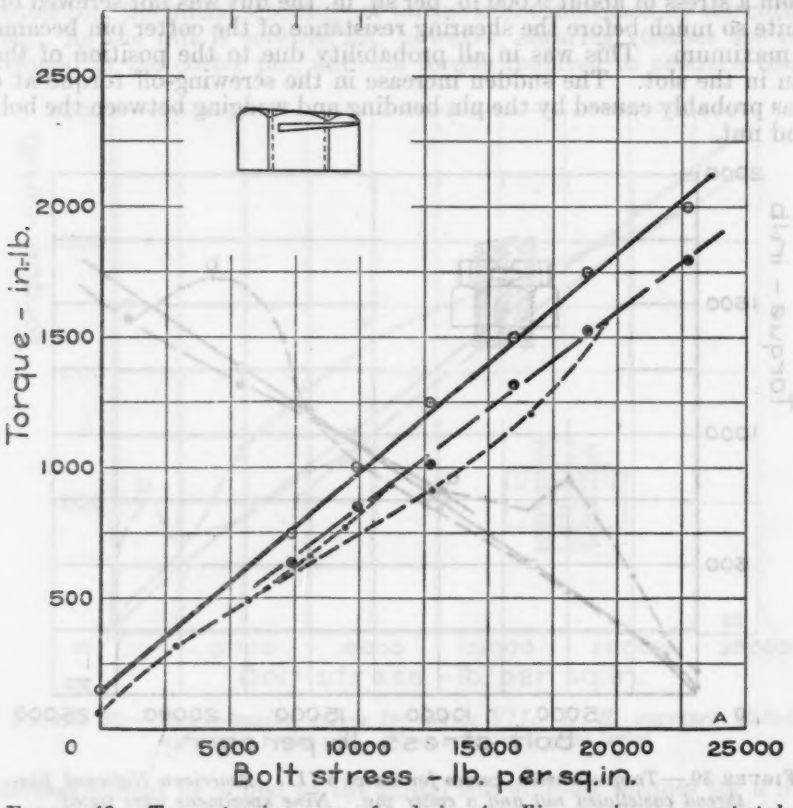

FIGURE 40.—*Torque-tension curves for device A. Five specimens were tested*

at *b* (fig. 39) was appreciably higher than the initial screwing-off torque. However, it seems evident that if the cotter pin had been a snug fit in the slot the maximum torque would have been somewhat higher.

Device A (fig. 40).

The curves for this device are similar to those for device *II* except that the torque (about 150 in. lb.) required to screw-on the nut raised the screwing-on curve by this amount. The differences between the screwing-on and the screwing-off curves are about the same as for device *II*. This curve intersects the axis of zero stress at about 75 in. lb. showing that the nut had been permanently deformed and that

the torque required to screw on the same nut would thereafter be about 75 in. lb. instead of 150 in. lb.

Devices B and B–U. S. (figs. 41 and 42).

As the only difference in these devices was the width across the flats of the hexagon of the nut, they will be discussed together.

The screwing-on and the screwing-off torques are proportional to the stress up to *a*, when the stress is about 10,000 lb. per sq. in. The differences in the stress at *a*, Figures 41 and 42, for the two devices,

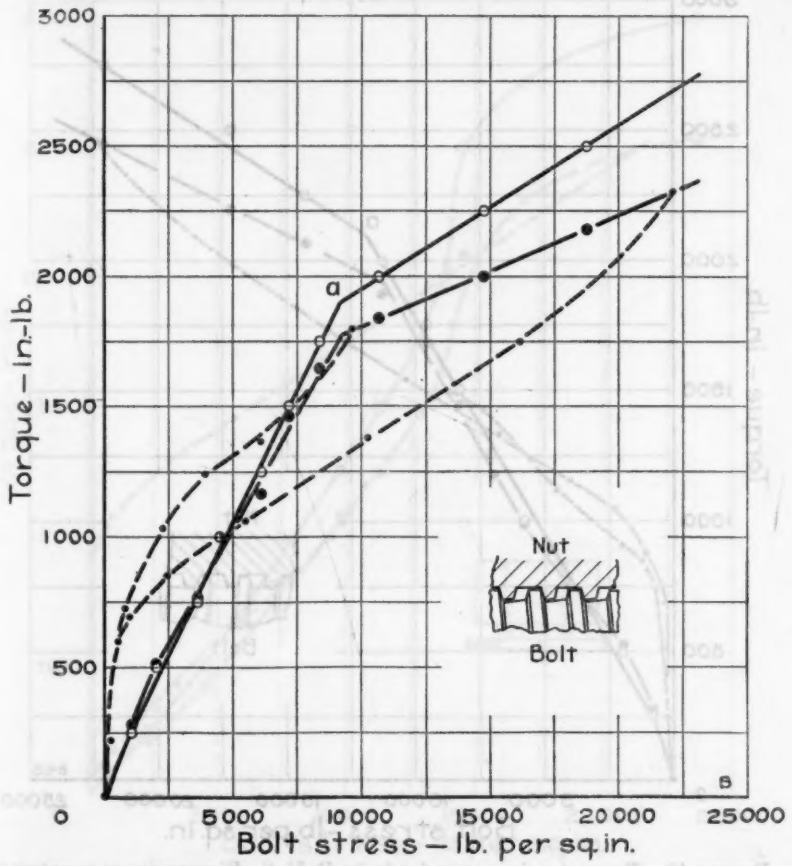

FIGURE 41.—*Torque-tension curves for device B. Five specimens were tested*

are probably due to small differences in the dimensions of the specimens. For stresses above *a* there is a straight-line relation between torque and stress for both screwing on and screwing off, and the lines intersect the axis of zero stress at about the same point.

From zero to the point *a* on these graphs only the helical cones are in contact, and both the screwing-on and screwing-off torques increase very rapidly as the stress increases, due to the friction between the helical cones. The curves for continuous screwing off from stresses close to or below *a* show that the torque is considerably greater than either the screwing-on or the initial screwing-off torque for the same

stress. The change in the slope of the screwing-on and the initial screwing-off curves at *a* is caused by the thrust faces *c* in Figure 2 coming into contact. As the stress is increased above the value at *a*, the compressive forces on these thrust faces increase, but the compressive forces on the helical cones are practically unchanged. The curves for continuous screwing off from stresses higher than those at *a*, lie below those for both screwing-on and initial screwing-off until they cross these curves between zero and *a*. For stresses below 5,000

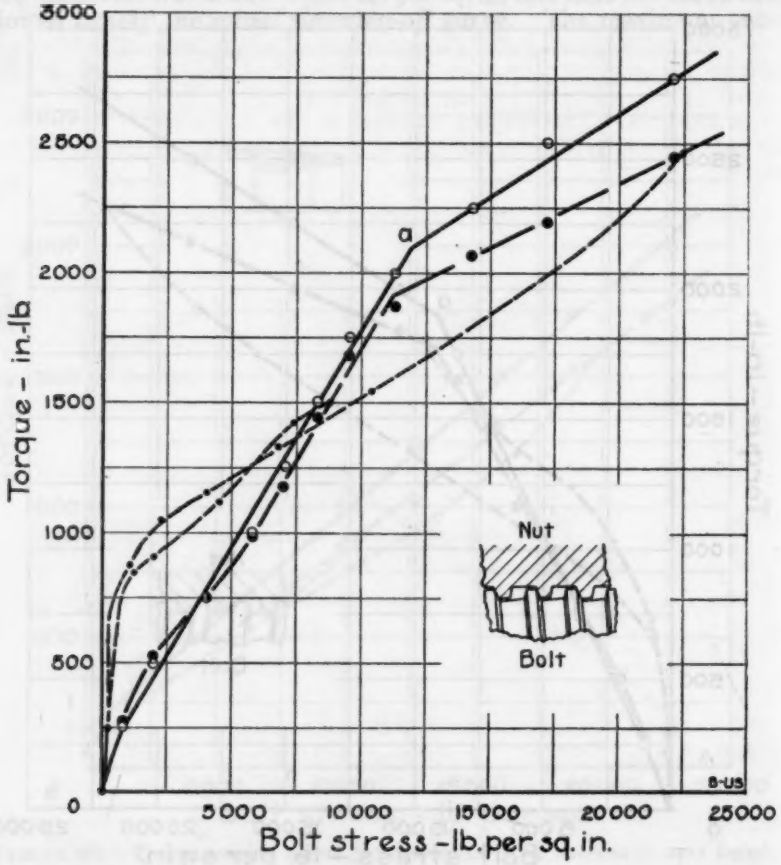

FIGURE 42.—*Torque-tension curves for device B–U. S. Five specimens were tested*

lb. per sq. in. these torques are much greater than the screwing-on torques or the initial screwing-off torques. As the stress is further decreased they coincide approximately with the curves for screwing-off to zero from stresses below *a*.

Device C (fig. 43).

As the stress increases to 15,000 lb. per sq. in., the screwing-on and initial screwing-off torques for this device increase more rapidly than the stress, being much greater than those for devices *I* and *II* (figs. 32 and 33, regular nuts). The initial screwing-off torques are always less than the screwing-on torques, the difference increasing as the

stress increases. For stresses above 15,000 lb. per sq. in., the torques increase much less rapidly. Probably the washer, *b*, Figure 3, came into contact with the face of the nut. Higher stresses, therefore, did not increase the forces acting at *a*.

The curve for screwing off to zero from 10,000 lb. per sq. in, coincides approximately with the initial screwing-off curve. But for continuous screwing off from about 22,000 lb. per sq. in., most of this curve lies above both the screwing-on and initial screwing-off curves. It is approximately parallel to the corresponding curve for device *II*,

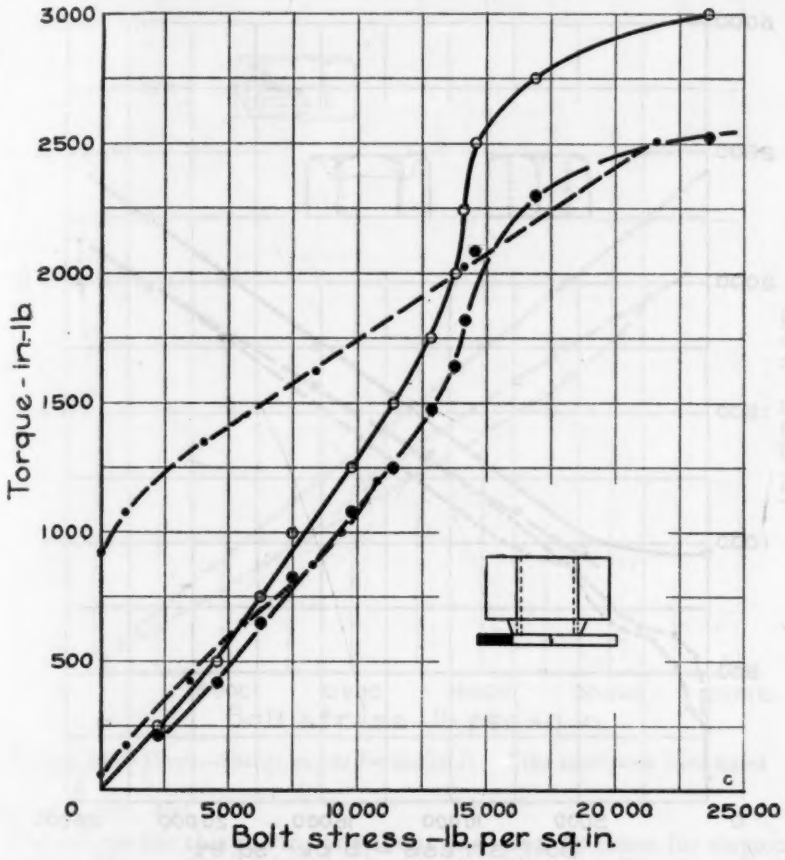

FIGURE 43.—*Torque-tension curves for device C. Five specimens were tested*

but lies about 1,000 inch-pounds higher. It is evident that the angle of the tapered portion of the nut is below the angle of friction, so that when continuously screwing off from high stresses, the washer *b*, Figure 3, continues to exert large forces at *a*, as the stress decreases. The torque required to rotate the nut when the stress was zero was about 1,000 inch-pounds.

Both the screwing-on and the initial screwing-off torques for this device at a stress of 20,000 lb. per sq. in. are approximately 1,000 inch-pounds greater than for devices *I* and *II*, Figures 32 and 33 (regular nuts).

Device D (fig. 44).

For this device, except for low stresses, there is a straight-line relation between the stress and the screwing-on and the initial screwing-off torques. These curves, if projected, intersect the axis of zero stress at the same point, about 700 inch-pounds. They are roughly parallel to the corresponding curves for device *II*, U. S. standard nut, but 700 inch-pounds higher. The torque required to rotate the nut under zero stress was initially about 900 inch-pounds, but after the stress had been increased to 5,000 lb. per sq. in. this value decreased

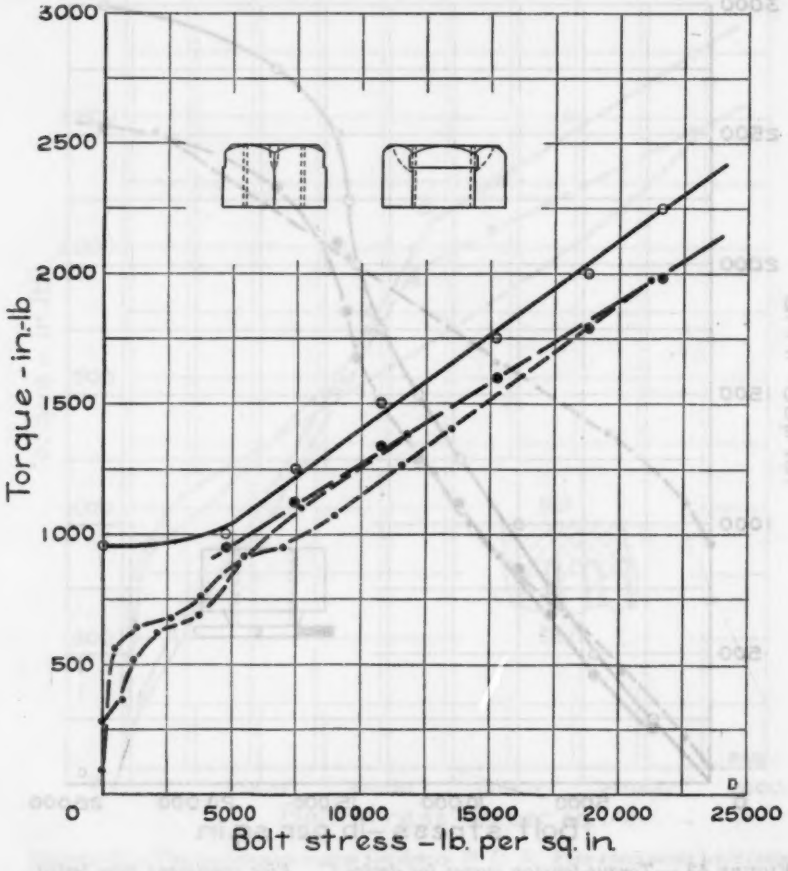

FIGURE 44.—*Torque-tension curves for device D. Five specimens were tested*

to about 700 inch-pounds, because the initial screwing-off curve intersects the axis at this point.

The curve for continuous screwing off from a stress of about 12,000 lb. per sq. in. followed the initial screwing-off curve, then decreased rapidly at low stresses. The curve for continuous screwing off from a stress of about 22,000 lb. per sq. in., if projected, intersects the axis of zero stress at about 400 inch-pounds. The curve indicates that both the nut and the bolt were permanently deformed after the test, the initially deformed portion of the nut being expanded, as shown

by the lower intercept, and the bolt becoming somewhat tapered, as shown by the rapid decrease of the torque near zero stress. This interpretation was confirmed by supplementary measurements obtained by screwing the device on and off an unstressed bolt.

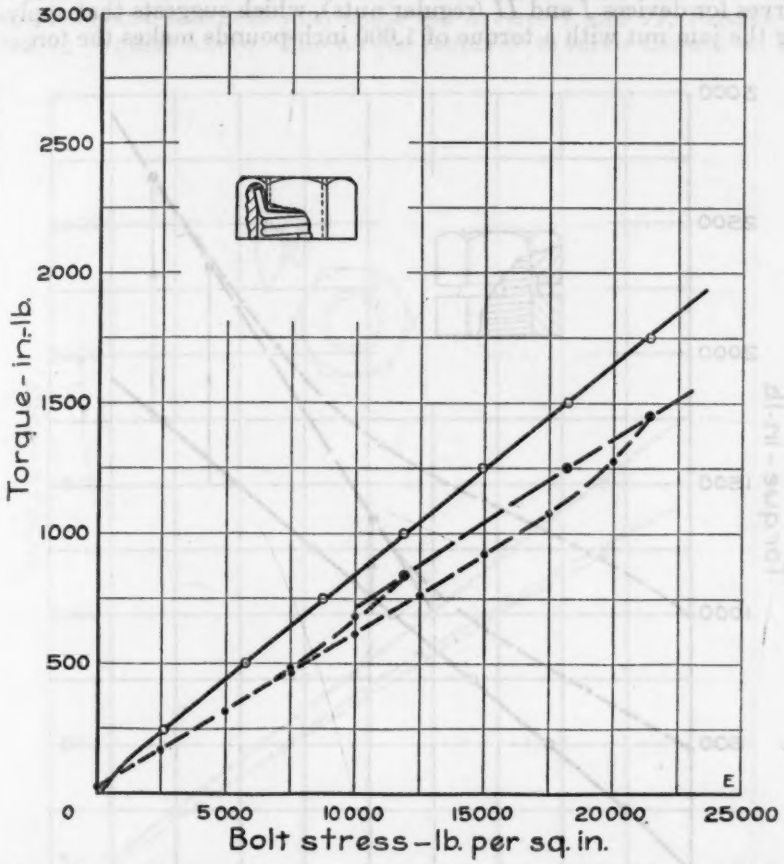

FIGURE 45.—*Torque-tension curves for device E. Nine specimens were tested*

Device E (fig. 45).

The curves for this device are about the same as those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The screwing-on and the initial screwing-off torques are approximately proportional to the stress.

The end *b* of the spring, Figure 5, was deformed when the device was unscrewed. It could not be used again.

Device F (fig. 46).

The screwing-on torques for this device, as should be expected, were proportional to the stress and the values the same as for those of devices *I* and *II*, Figures 32 and 33 (regular nuts). The initial screwing-off torques are considerably greater than the screwing-on

torques for corresponding stresses, because screwing on the jam nut *d*, Figure 6, after the nut *a* has been tightened increased the frictional resistance.

The curves for continuous screwing off lie considerably above the other curves. They are roughly parallel to the initial screwing-off curves for devices *I* and *II* (regular nuts), which suggests that applying the jam nut with a torque of 1,000 inch-pounds makes the torque

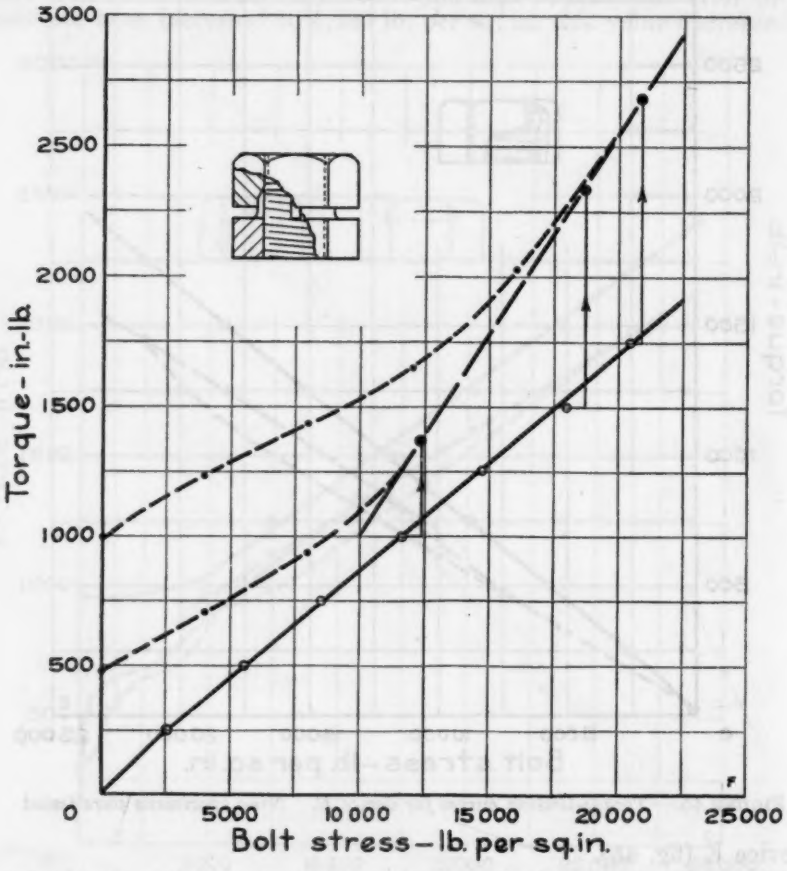

FIGURE 46.—*Torque-tension curves for device F. Nine specimens were tested*

required to rotate the nut under zero stress about 500 inch-pounds, and, applying it with a torque of 1,750 inch-pounds, makes this torque about 1,000 inch-pounds. The initial screwing-off torques are about these amounts greater than those for devices *I* and *II* (regular nuts). The threads in the nuts were not a snug fit on the bolt threads. Therefore it was necessary to deform the cylindrical portion of the nut appreciably before the threads were in contact and the frictional resistance to rotation increased. Apparently the threads came into contact when the torque on the jam nut was about 750 inch-pounds.

There is a straight-line relation between the stress and the initial screwing-off torque for stresses above this value.

Device G (fig. 47).

The curves for this device are, except for a small torque at zero stress, almost identical with those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The torque required to screw the nut on the

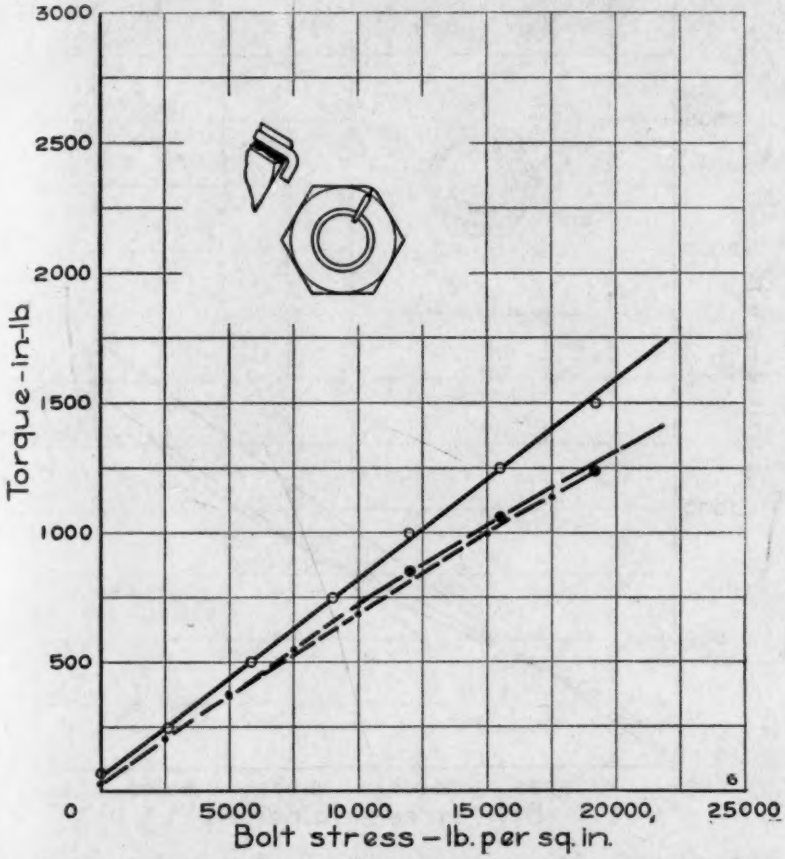

FIGURE 47.—*Torque-tension curves for device G. Nine specimens were tested*

bolt was initially about 100 inch-pounds. The pin *b*, Figure 7, cut a small chip off the tops of the bolt threads. When the nut was screwed off the pin was bent away from the bolt. When the nut was continuously screwed off, the torque required to rotate the nut at zero stress was about 50 inch-pounds. Apparently the screwing-on torques were about 100 inch-pounds greater than those for regular nuts and the screwing-off torques about 50 inch-pounds greater.

Device H (fig. 48).

The curves for this device are somewhat lower than those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The screwing-on torques are proportional to the stress.

The initial screwing-off torques were about the same amount less than the screwing-on torques as those for the regular nuts.

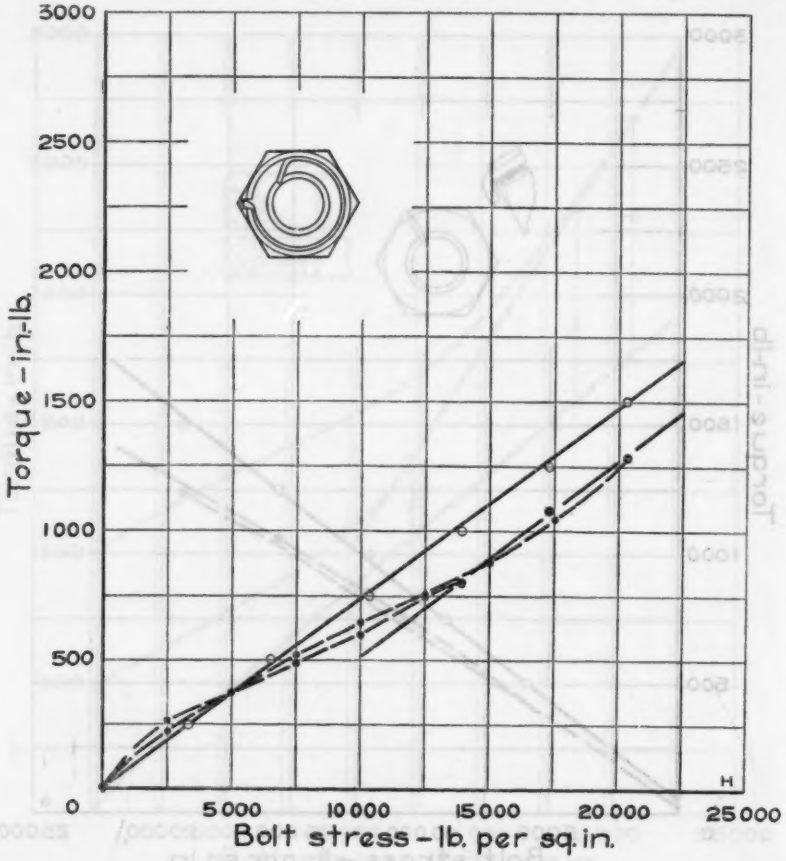

FIGURE 48.—*Torque-tension curves for device H. Eleven specimens were tested*

When the nut was screwed off, the end of the spring *c*, Figure 8, cut into the bolt threads, and after the device was removed from the bolt it was found that this end of the spring had bent into a circular arc, making it necessary to insert a new spring in the nut, if the device was to be used again.

Device I (fig. 49).

The screwing-on and initial screwing-off curves for this device are, as should be expected, almost identical with those for devices *I* and *II*, Figures 32 and 33 (regular nuts). When the device applied as in these tests was continuously screwed off from a stress of about 12,000

lb. per sq. in. the torque was about 150 inch-pounds at zero stress, and about 350 inch-pounds at zero stress when the device was continuously screwed off from a stress of about 20,000 lb. per sq. in. If it had been screwed on either more or less than the half turn recommended, these torques would have had different values. When screwing off, the torque was applied to the regular nut only. As the device did not rotate, this deflected the segments of the thread until they

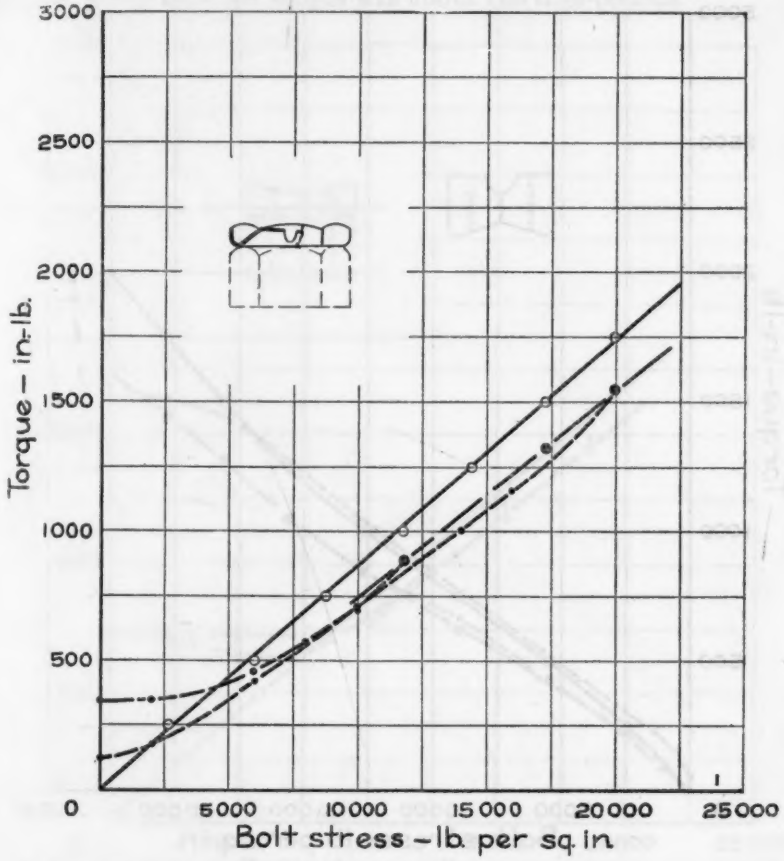

FIGURE 49.—*Torque-tension curves for device I. Nine specimens were tested*

were firmly seated between the threads of the bolt as the stress approached zero. When the device was removed from the bolt it was found that the threads of the bolt had been sheared by the thread in the device. This, of course, would not occur if the jam nut were removed first.

Device J (fig. 50).

The screwing-on and the initial screwing-off torques for this device were about the same as those for devices *I* and *II*, Figures 32 and 33

regular nuts), but they were not proportional to the stresses, tending at high stresses to increase more rapidly than the stress because of the deformation of the nut.

The curve for continuous screwing off from a stress of about 12,000 lb. per sq. in. almost coincides with the initial screwing-off curve, indicating that the deformation of the device at this stress was not sufficient to affect the torques appreciably.

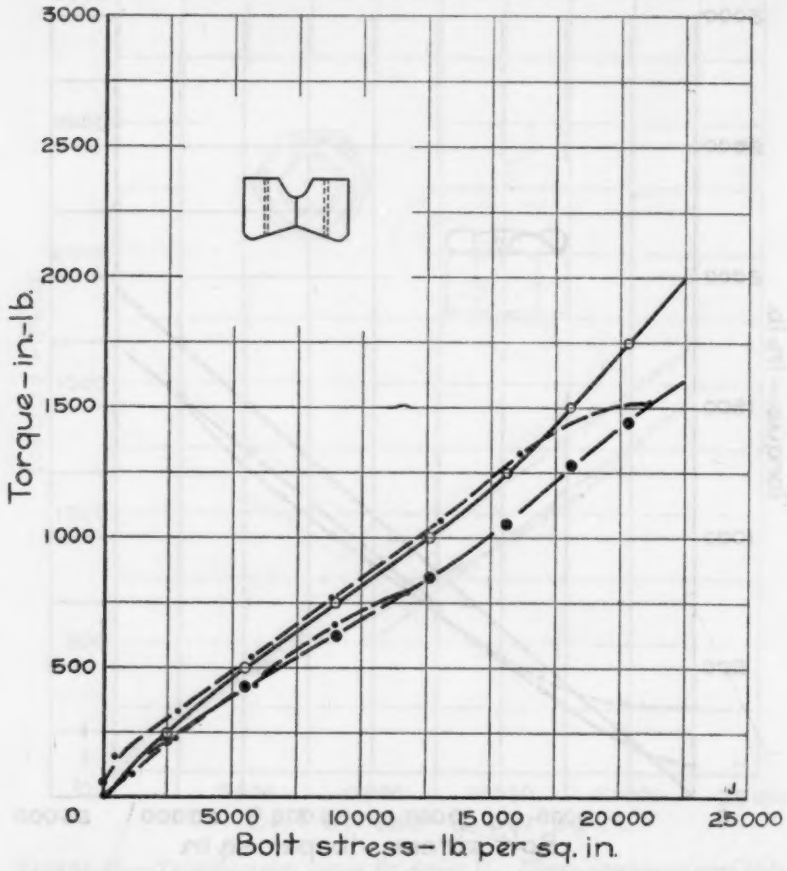

FIGURE 50.—*Torque-tension curves for device J. Five specimens were tested*

The curve for continuous screwing off from a stress of about 21,000 lb. per sq. in. lies slightly above the screwing-on curve, the torque being about 100 in. lb. when the stress became zero, indicating that the deformation of the device at stresses above 15,000 lb. per sq. in. was sufficient to increase both the screwing-on and the screwing-off torques.

As the stress decreased the deformation decreased, but when the stress became zero the torque was still about 100 in. lb., showing that the device was permanently deformed.

Device K (fig. 51).

The screwing-on curve for this device is, as should be expected, identical with those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The initial screwing-off torques were proportional to the stresses. At first the two curves for continuous screwing off coincide approximately with the initial screwing-off curve but for stresses below about 8,000 lb. per sq. in. become almost horizontal. When the stress was zero the torque was about 700 inch-pounds.

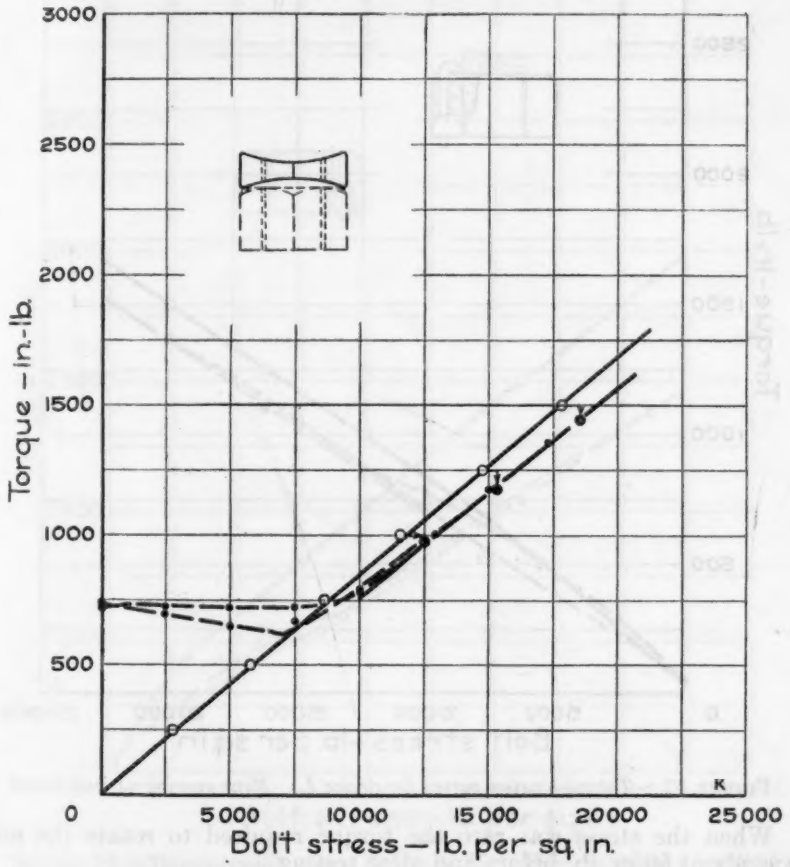

FIGURE 51.—*Torque-tension curves for device K. Nine specimens were tested*

When the regular nut was continuously screwed off this device did not rotate on the bolt until the stress was about 8,000 lb. per sq. in. It deformed until the face in contact with the regular nut was approximately flat. As the stress decreased below this value the device rotated with the regular nut.

When the device was removed from the bolt it was found that the surface which had been in contact with the regular nut remained nearly flat, indicating that the device had been permanently deformed.

Device L (fig. 52).

Except for the small torques at zero stress these curves are similar to those for devices *I* and *II*, Figures 32 and 33 (regular nuts), but show somewhat lower torques.

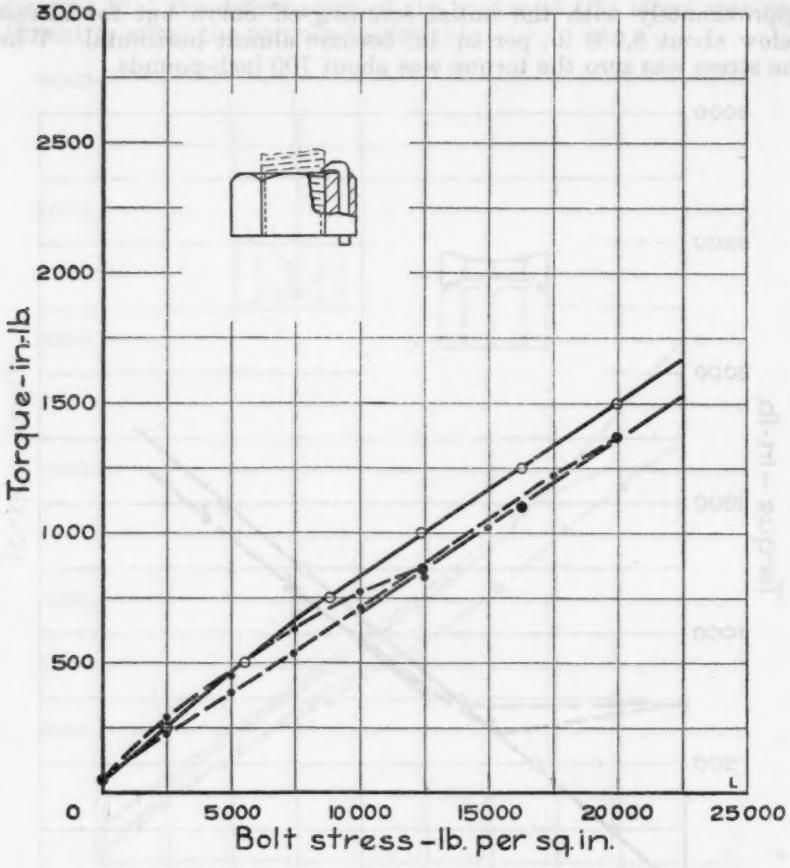

FIGURE 52.—*Torque-tension curves for device L. Nine specimens were tested*

When the stress was zero the torque required to rotate the nut was about 50 in. lb. before and after testing.

When the device was removed from the bolt it was found that the bolt threads had been roughened by the pin in the device.

Device M (fig. 53).

At a stress of about 22,000 lb. per sq. in. the screwing-on torque for this device was the same as those for devices *I* and *II*, Figures 32 and 33 (regular nuts), but for most stresses between this value and zero the screwing-on torque was about 150 inch-pounds greater.

The initial screwing-off torques at about 20,000 lb. per sq. in. were about 100 inch-pounds lower than those for regular nuts, the

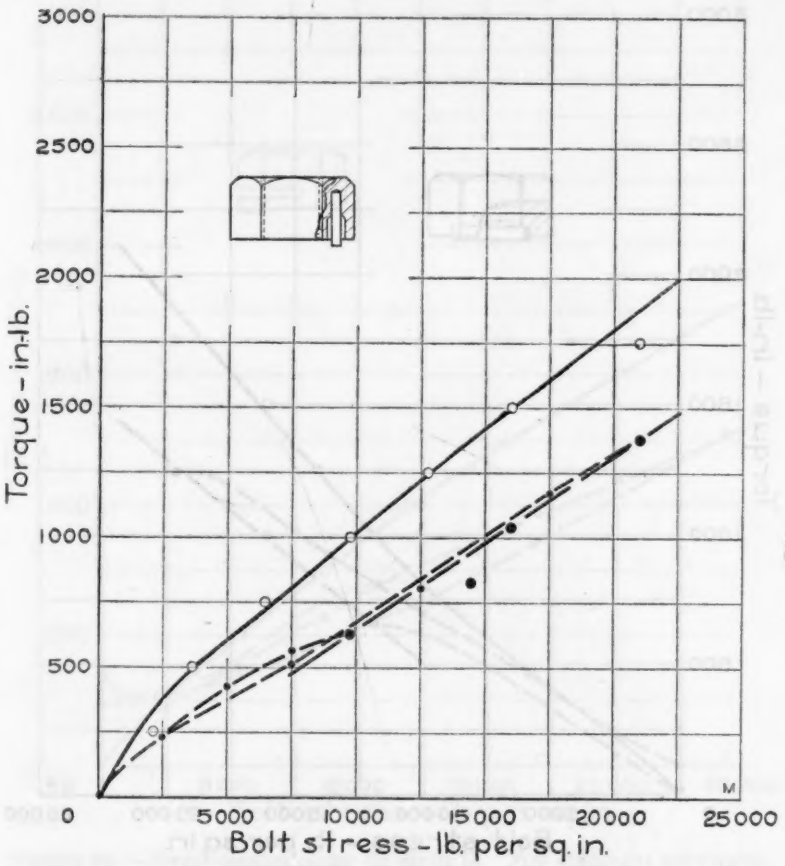

FIGURE 53.—*Torque-tension curves for device M. Nine specimens were tested*

torque being proportional to the stress. The continuous screwing-off torques lie slightly above the initial screwing-off torque curve extended.

When this device was removed from the bolt it was found that the pin in the device had cut into the face of the bearing washer. Chips filled the space around the pin. It would be necessary to remove them before using the device again.

Device N (fig. 54).

The screwing-on torques for this device were almost the same as those for devices *I* and *II*, Figures 32 and 33 (regular nuts), up to a stress of about 13,000 lb. per sq. in. Above this value these torques increased more rapidly as the stress increases.

The initial screwing-off torques were about 150 inch-pounds less than those for regular nuts, but the torques for continuous screwing

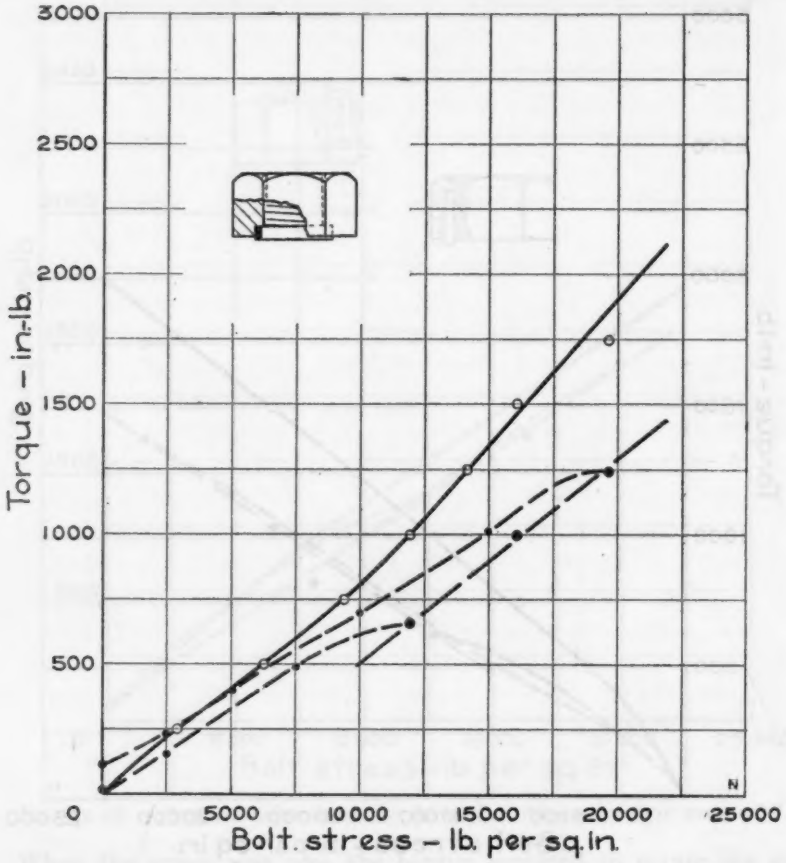

FIGURE 54.—*Torque-tension curves for device N. Nine specimens were tested*

off were only slightly less. When continuously screwed off from a stress of 20,000 lb. per sq. in. the torque at zero stress was about 100 inch-pounds.

When the device was removed from the bolt the ring usually remained on the bolt. To remove it the ends of the strip forming the ring were pried apart with a screw driver. A new copper ring would be needed each time the device was used.

Device O (fig. 55).

The screwing-on torques for this device are slightly greater than those for devices *I* and *II*, Figures 32 and 33 (regular nuts), up to about 10,000 lb. per sq. in. For higher stresses they increase less rapidly, until at 20,000 lb. per sq. in. stress they are lower than for devices *I* and *II*.

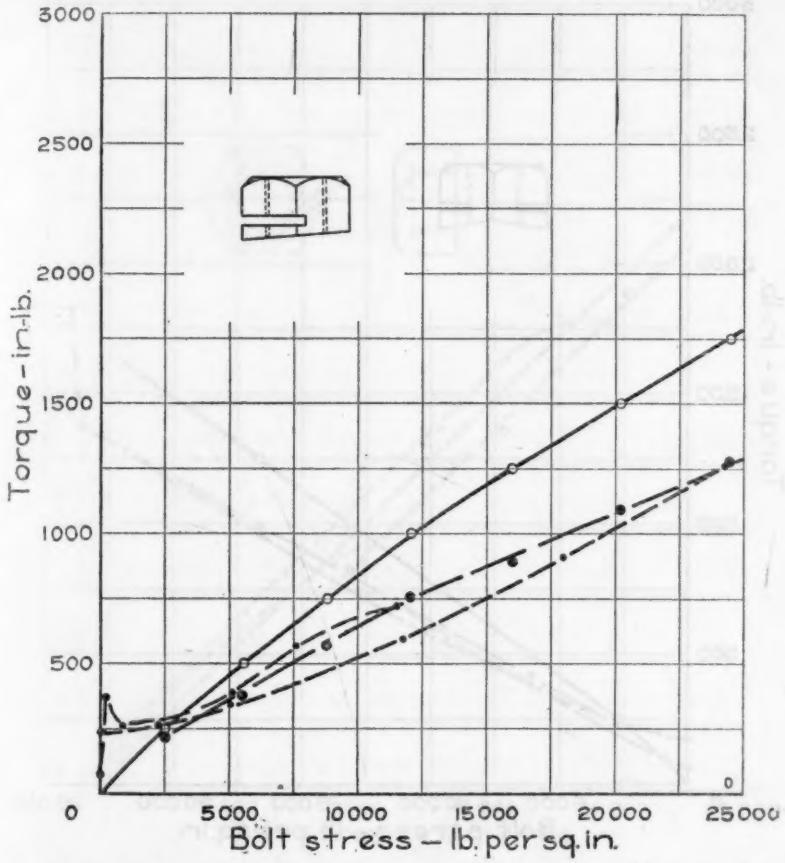

FIGURE 55.—*Torque-tension curves for device O. Five specimens were tested*

For high stresses the initial screwing-off torques are considerably less than those for regular nuts.

In continuous screwing off there is still a torque at zero stress, indicating that the device has been permanently deformed after it has been stressed as high as 10,000 lb. per sq. in.

Device P (fig. 56).

The screwing-on and initial screwing-off torques were somewhat lower than for devices *I* and *II*, Figures 32 and 33 (regular nuts).

In continuous screwing off there was still a torque at zero stress, indicating that the device was permanently deformed after it had been stressed as high as 10,000 lb. per sq. in.

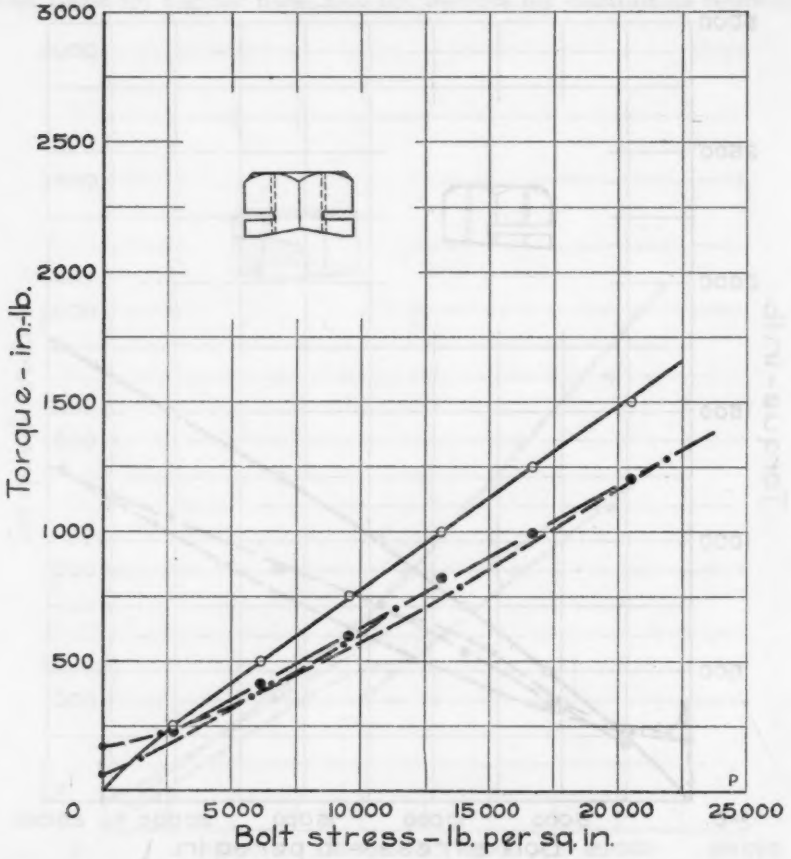

FIGURE 56.—*Torque-tension curves for device P. Five specimens were tested*

Device Q (fig. 57).

The screwing-on torques for this device are considerably greater than those for devices *I* and *II*, Figures 32 and 33 (regular nuts). They are, as should be expected, proportional to the stresses. The initial screwing-off torques are only slightly less than the screwing-on

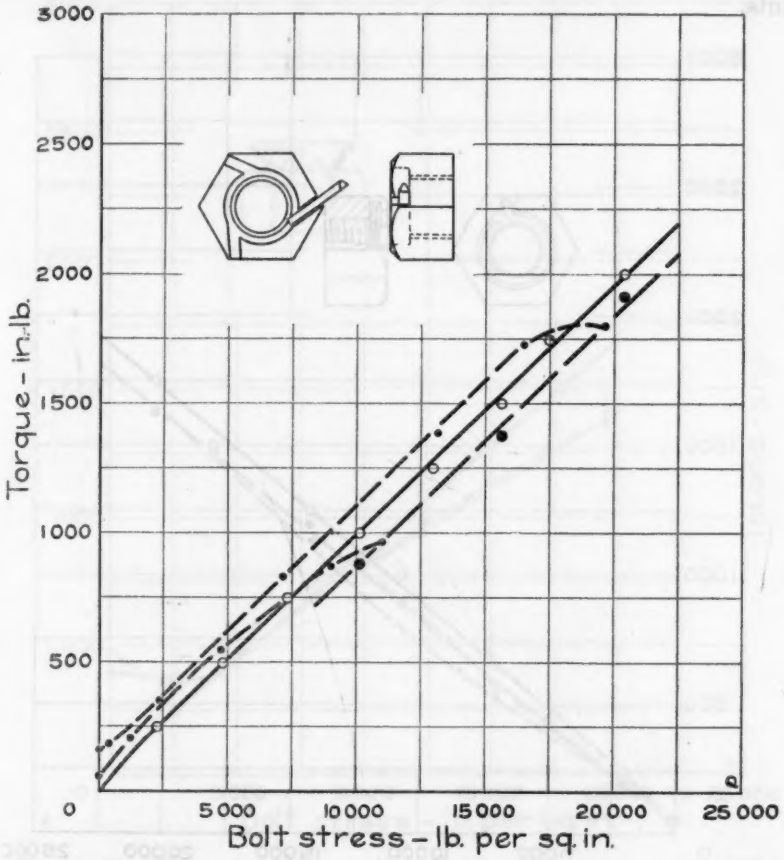

FIGURE 57.—*Torque-tension curves for device Q. Eleven specimens were tested*

torques. The torques for continuous screwing-off are about 100 inch-pounds greater than the screwing-on torque, this also being the value when the stress is zero.

This device can not be used unless there is sufficient room to insert the pin.

Device R (fig. 58).

The screwing-on torques for this device were about 50 inch-pounds greater than those for devices *I* and *II*, Figures 32 and 33 (regular nuts). In continuous screwing-off there was still a torque at zero stress.

Otherwise the curves are almost identical with those for regular nuts.

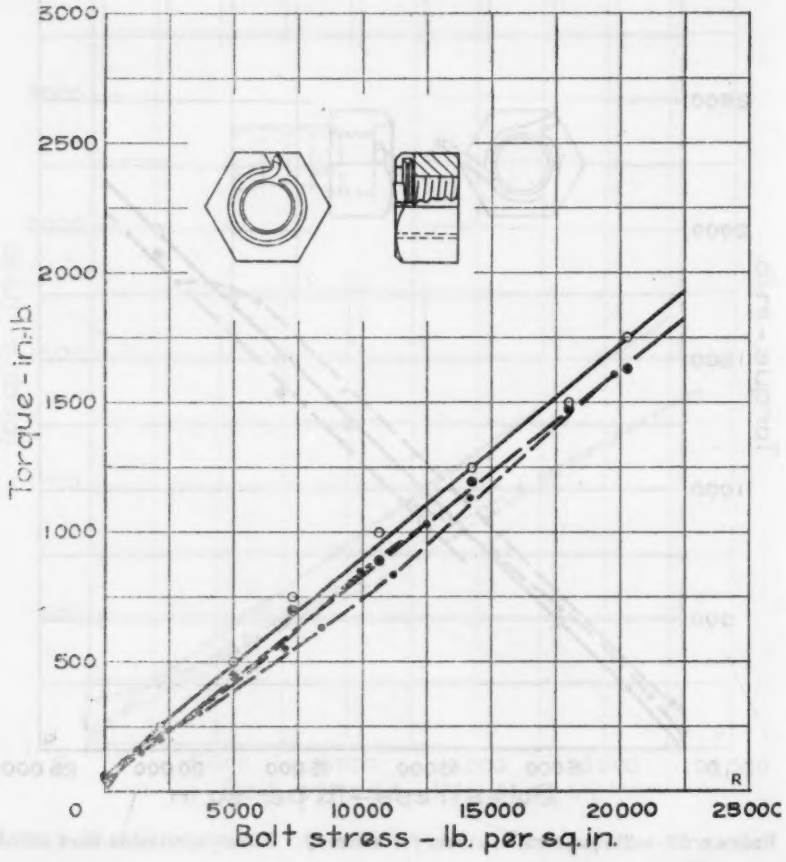

FIGURE 58.—*Torque-tension curves for device R. Five specimens were tested*

Device S (fig. 59).

The screwing-on and initial screwing-off torques for this device were about the same as those for devices *I* and *II*, Figures 32 and 33 (regular nuts). Application of the device after the regular nut was tightened increased the stress slightly.

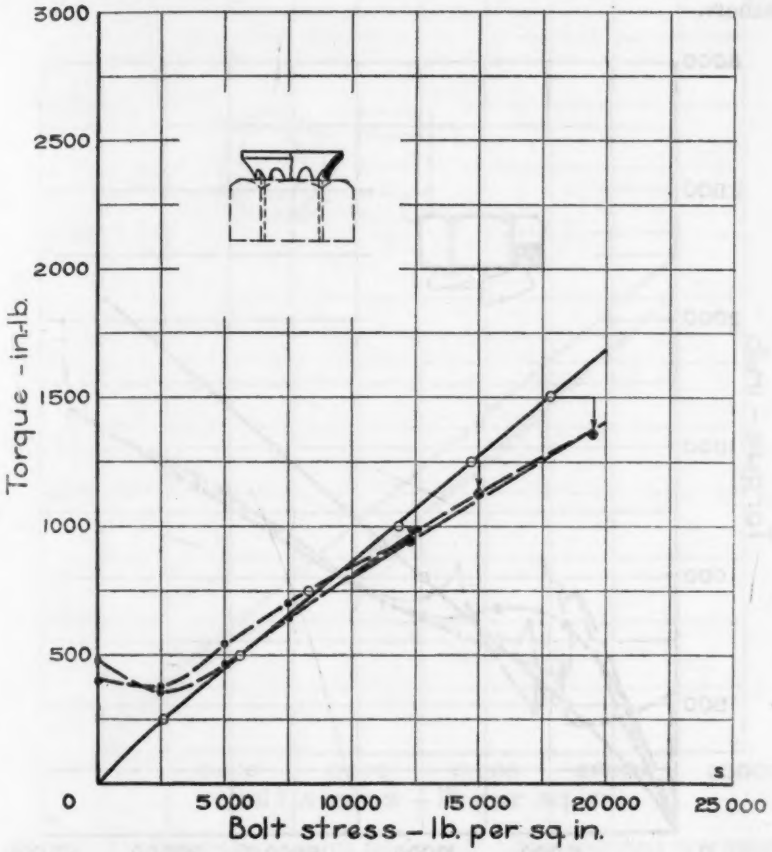

FIGURE 59.—*Torque-tension curves for device S. Nine specimens were tested*

For continuous screwing-off the torques were greater than the initial screwing-off torques, and for low stresses greater than the screwing-on torques. Below 3,000 lb. per sq. in. the torque increased to 400 or 500 inch-pounds at zero stress.

When the device was removed from the bolt it was found that the threads of the bolt had been roughened. As the device is permanently deformed when it is applied to the bolt, a new one must be used for each application.

Device T (fig. 60.).

The screwing-on torques for this device are greater than those for devices *I* and *II*, Figures 32 and 33 (regular nuts), being about 100 inch-pounds greater for a stress of 5,000 lb. per sq. in. and about 200 inch-pounds greater for a stress of 20,000 lb. per sq. in. The characteristic shape of this curve will be discussed later under lock washers.

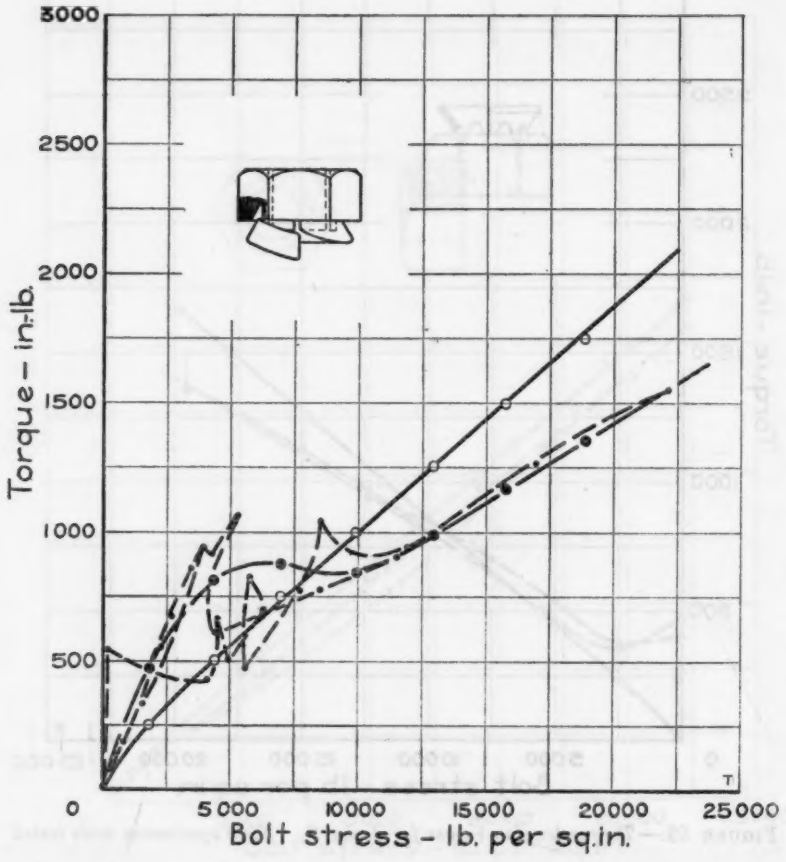

FIGURE 60.—*Torque-tension curves for device T. Five specimens were tested*

The initial screwing-off torques, however, are the same as those for regular nuts for high stresses, but are approximately 800 inch-pounds (considerably higher than the screwing-on torques) for stresses between 11,000 and 4,000 lb. per sq. in.

For continuous screwing-off, the torques are about the same as the initial screwing-off torques, but the values change greatly for small changes in stress below 10,000 lb. per sq. in.

When this device was removed from the bolt it was found that the device had cut into the face of the bearing washer and that the groove in the nut had been roughened.

The parts of this device, after test, are shown at T, Figure 76.

Device U (fig. 61).

The curves for this device are almost identical with those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The screwing-on torques are about 50-inch pounds higher and the initial screwing-off

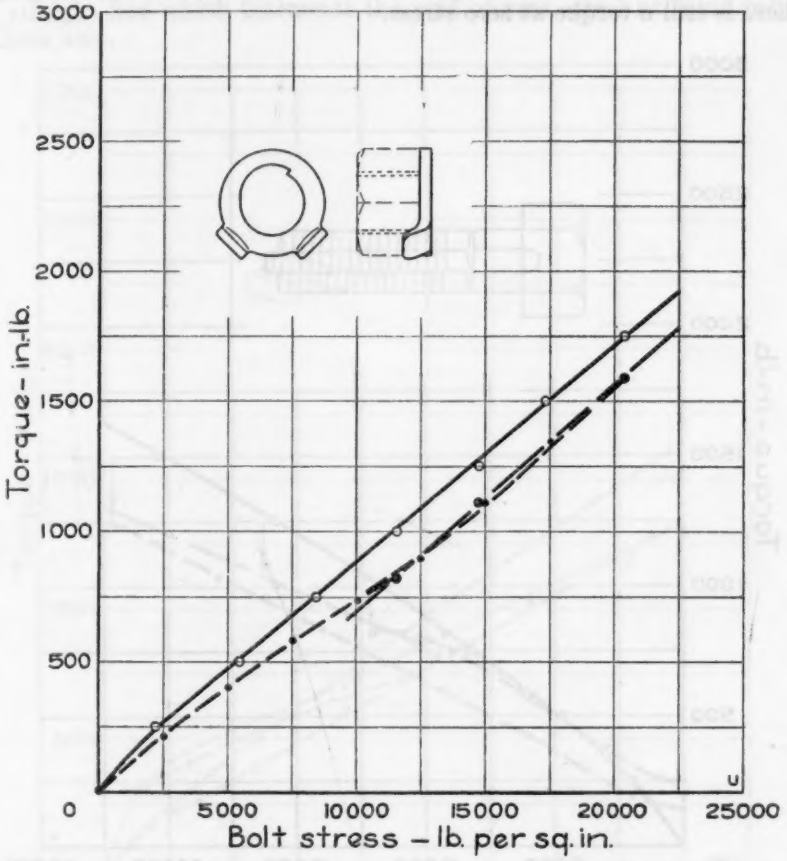

FIGURE 61.—*Torque-tension curves for device U. Nine specimens were tested*

torques about 100 inch-pounds higher at a stress of 20,000 lb. per sq. in.

When this device was removed from the bolt it was found that the threads of the bolt had been roughened.

Device V (fig. 62).

The screwing-on torques for this device are somewhat higher at low stresses and lower at high stresses than those for devices *I* and *II*, Figures 32 and 33 (regular nuts). The initial screwing-off torques are considerably lower at high stresses. In continuous screwing off there is still a torque at zero stress.

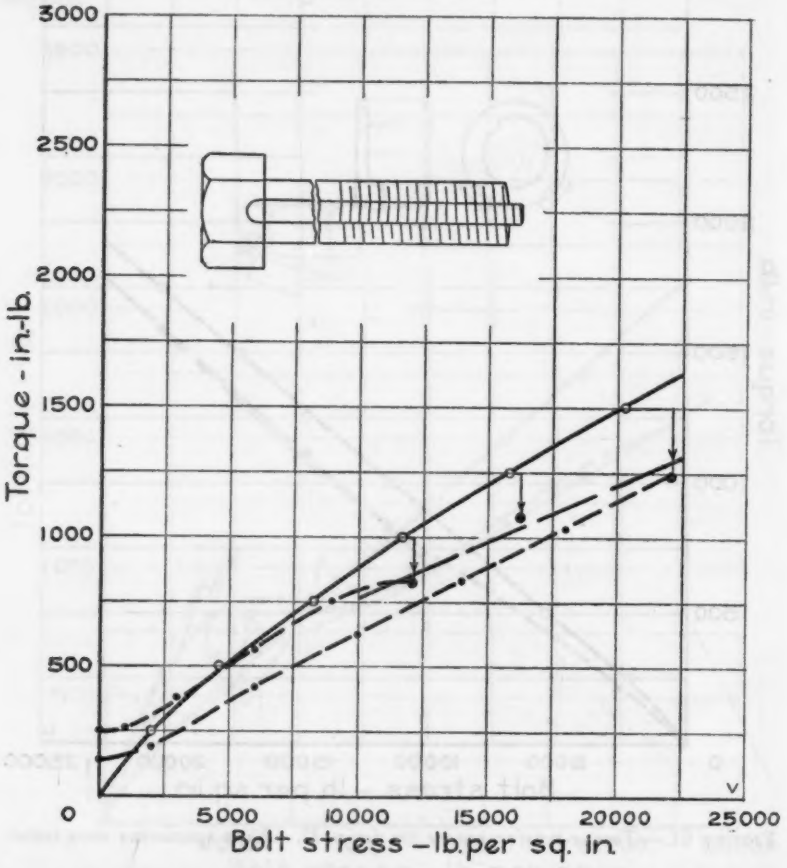

FIGURE 62.—*Torque-tension curves for device V. Nine specimens were tested*

As the key was bent over the nut when this device was applied, a new key was required for each application. When the nut was removed from this device it was found that the threads in the nut had been roughened.

Devices AA to JJ. Spring washers (figs. 63–72).

The screwing-on curves for the spring washers show a characteristic difference from the curves for regular nuts (*I*, *II*, and *III*).

The screwing-on torques, instead of being proportional to the stress, at first rise more rapidly, and in the majority of the cases approach a straight line which intersects the axis of zero stress at some point above zero.

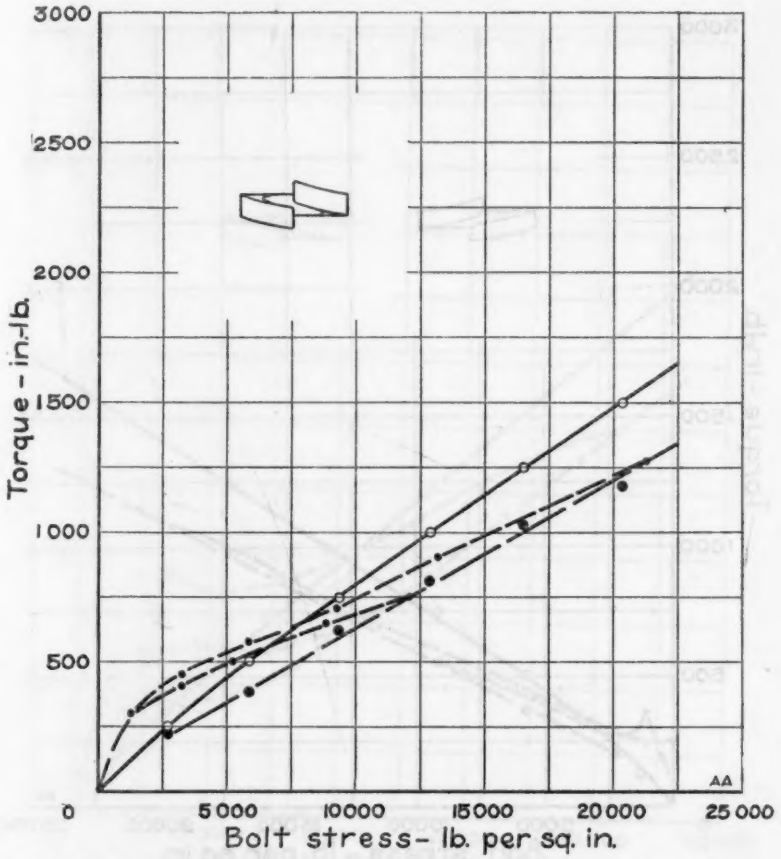

FIGURE 63.—*Torque-tension curves for device AA, spring washer. Five specimens were tested*

Comparison with the load-deflection curves, Figure 73, shows that in most cases the straight portion of the curve begins approximately at the load at which the washer became flat.

Thus for device EE, which is flat at loads corresponding to a stress in the bolt of less than 2,000 lb. per sq. in., the curve for screwing-on torque is straight above 5,000 lb. per sq. in., while for device DD, which is flat at 6,000 lb. per sq. in. stress, the curve is not straight until about 10,000 lb. per sq. in.

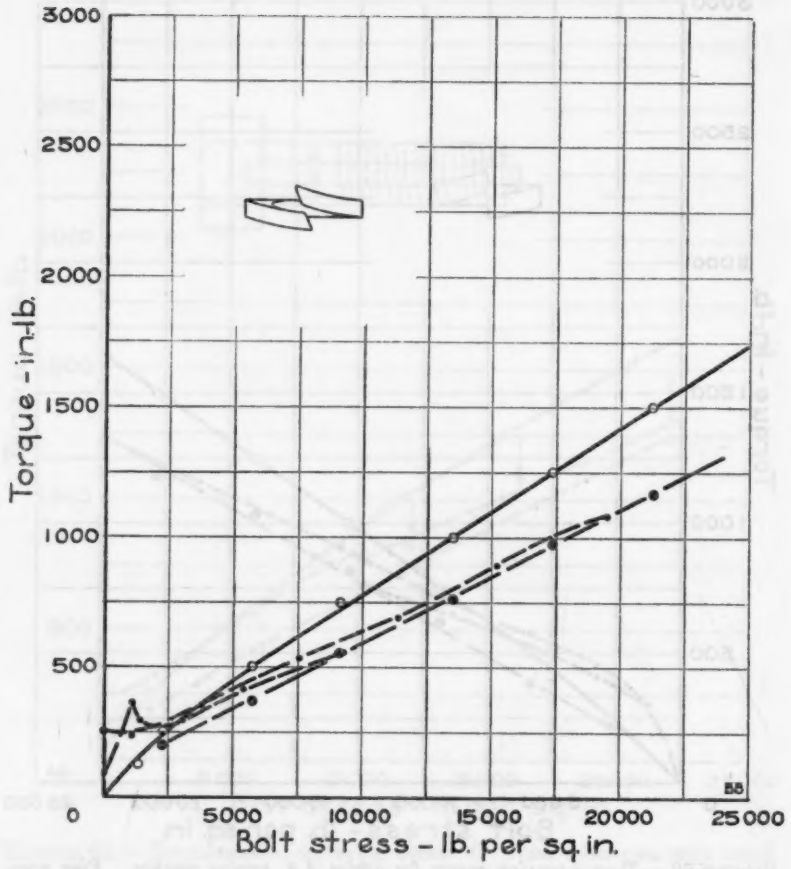

FIGURE 64.—*Torque-tension curves for device BB, spring washer. Five specimens were tested*

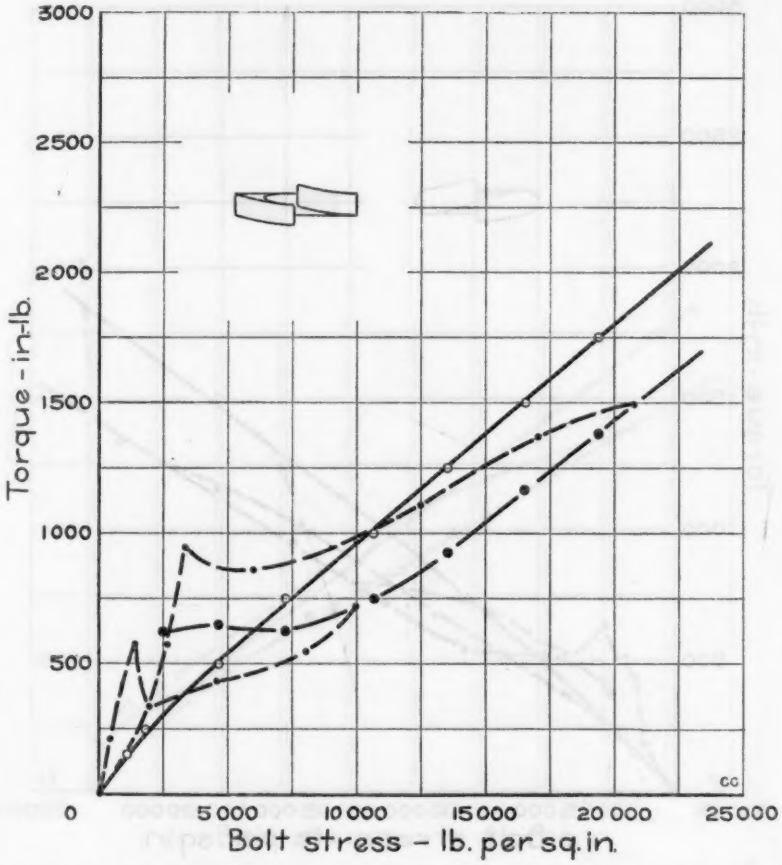

FIGURE 65.—*Torque-tension curves for device CC, spring washer. Five specimens were tested*

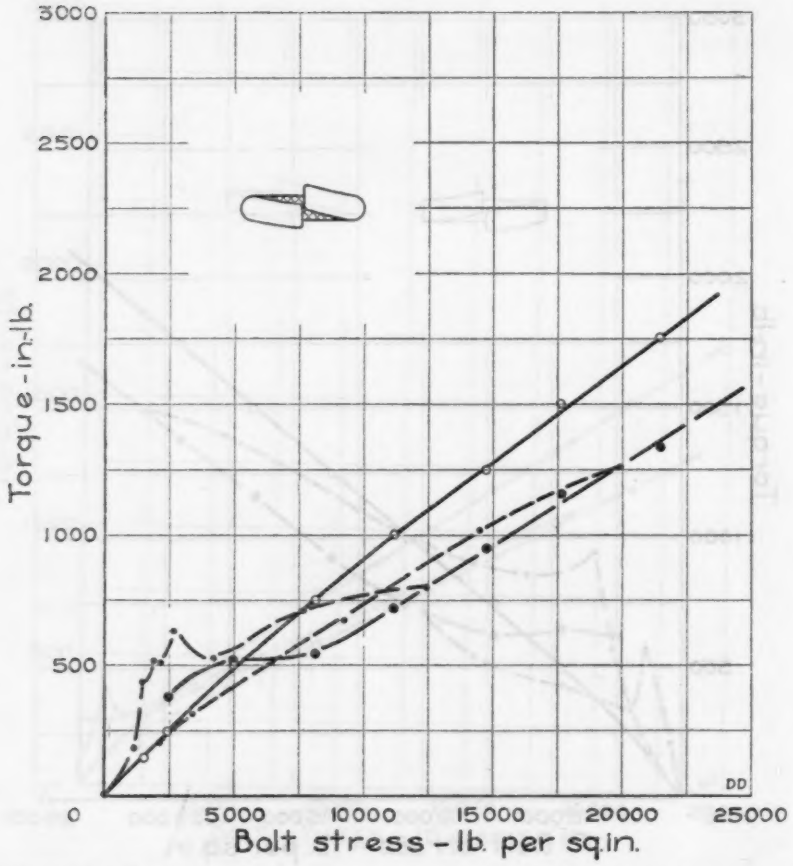

FIGURE 66.—*Torque-tension curves for device DD, spring washer. Five specimens were tested*

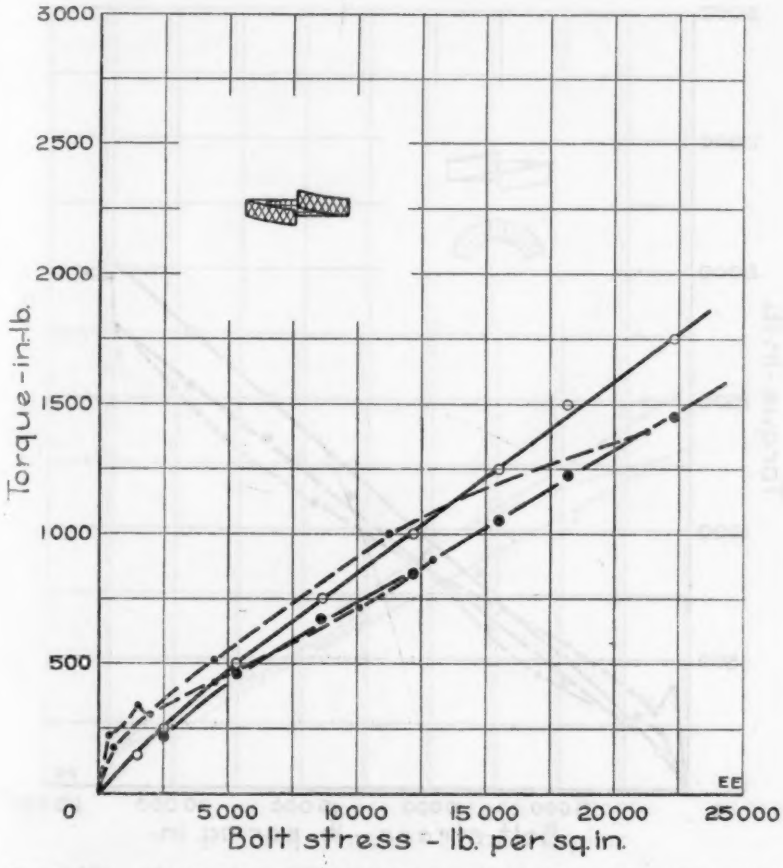

FIGURE 67.—*Torque-tension curves for device EE, spring washer. Five specimens were tested*

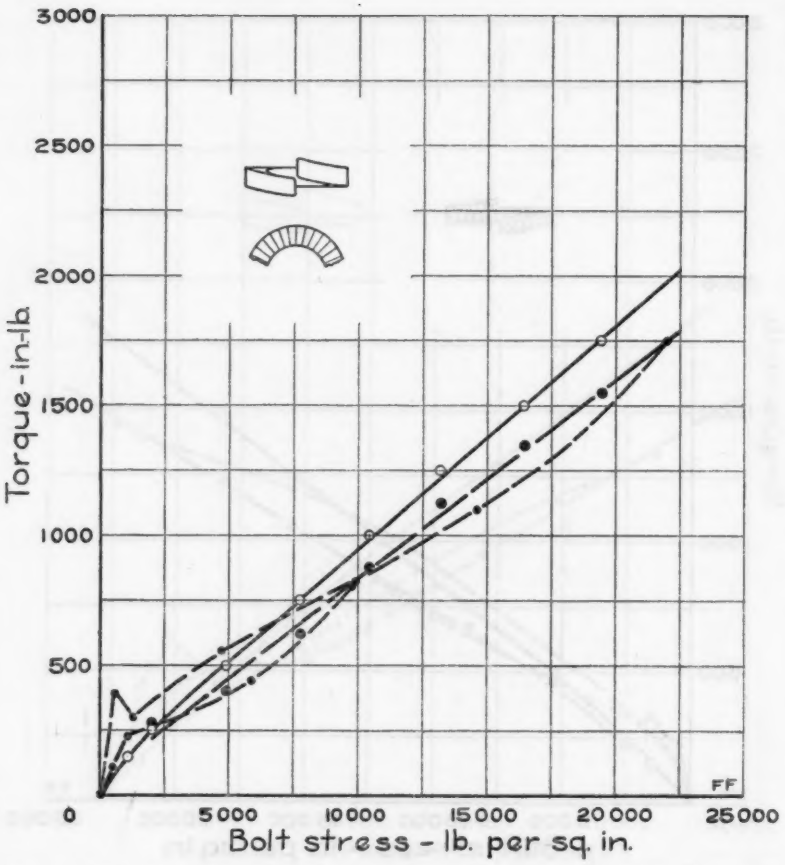

FIGURE 68.—*Torque-tension curves for device FF, spring washer. Five specimens were tested*

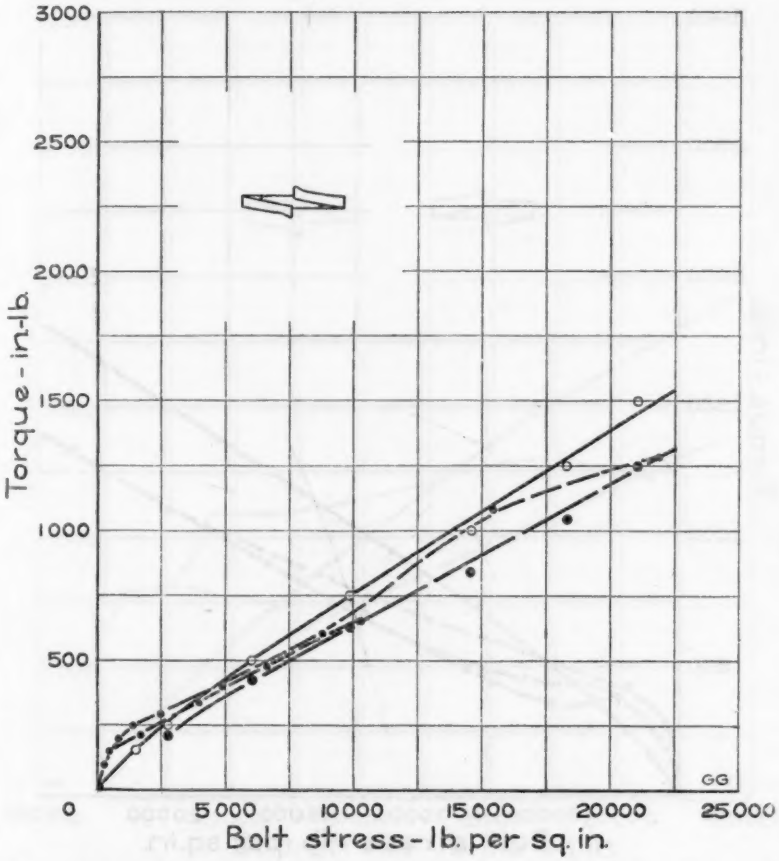

FIGURE 69.—*Torque-tension curves for device GG, spring washer. Five specimens were tested*

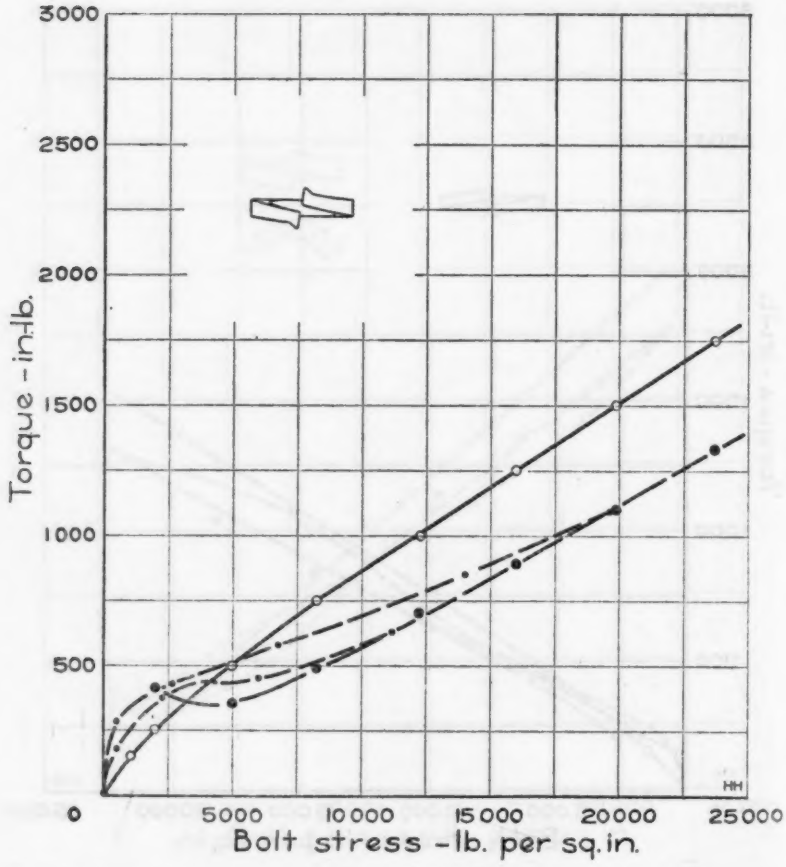

FIGURE 70.—*Torque-tension curves for device HH, spring washer. Five specimens were tested*

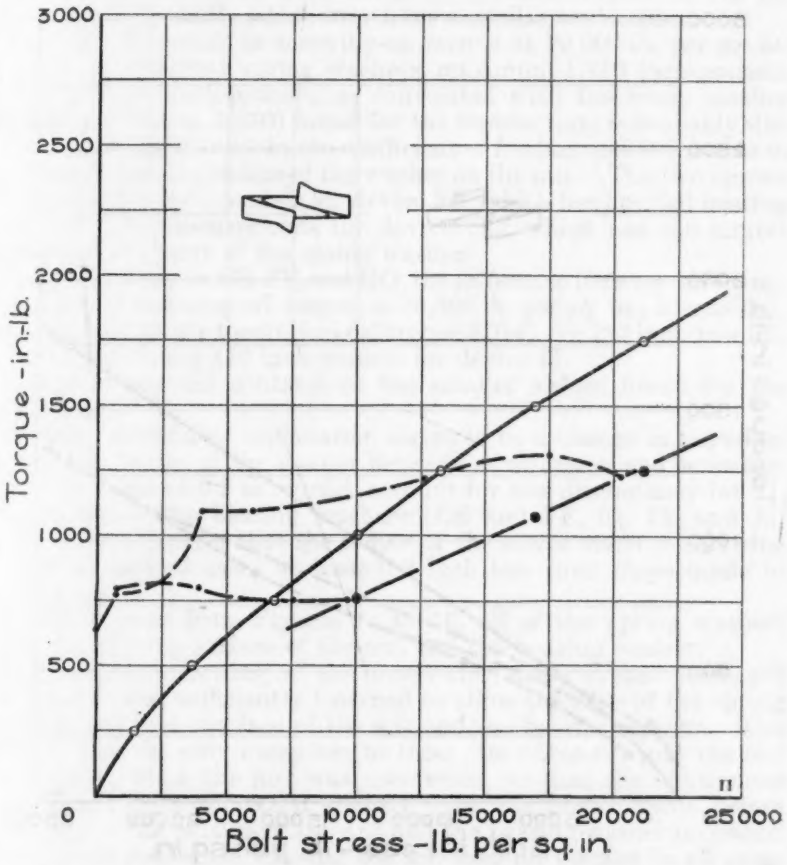

FIGURE 71.—*Torque-tension curves for device II, spring washer. Eleven specimens were tested*

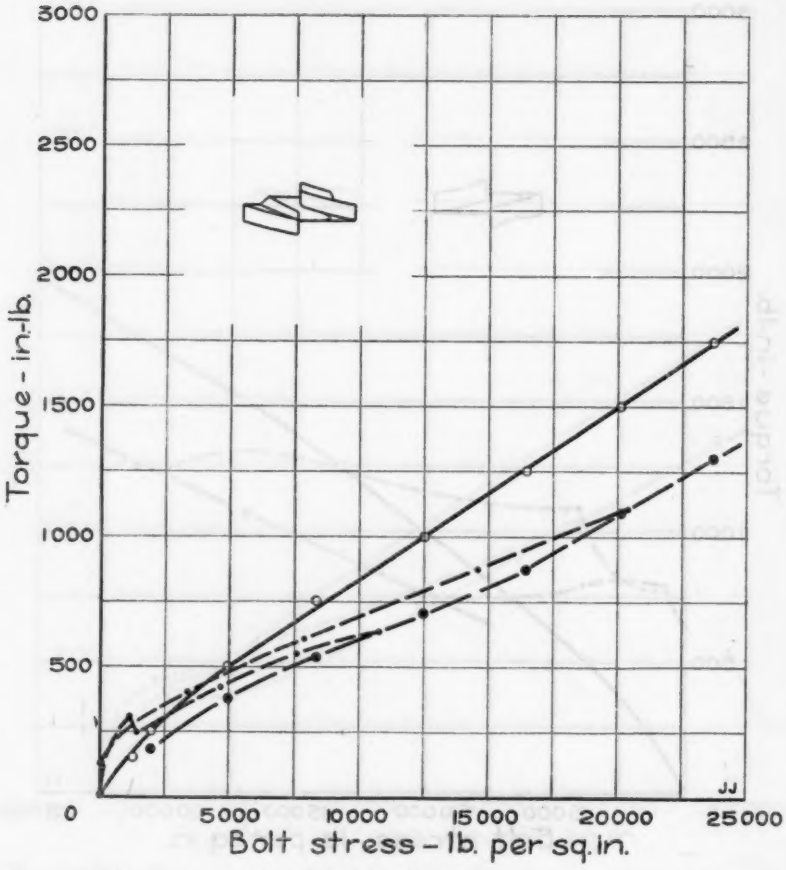

FIGURE 72.—*Torque-tension curves for device JJ, spring washer. Five specimens were tested*

It seems reasonable to ascribe this to the higher friction of the washer edges before they are pressed flat. This is further confirmed by the different shape of the curves for devices HH and II, Figures 70 and 71. These have stiff bent-up bearing edges which can not be pressed flat even at the highest stresses. The screwing-on curve for II does not become straight. This curve for HH does not become approximately straight until over 7,000 lb. per sq. in., although this washer is "pressed flat" (see fig. 73) at a stress of less than 2,000 lb. per sq. in. Similar characteristics were noted on the screwing-on curves for devices J, O, P, and T, which may have a similar explanation.

The large difference in screwing-on torque at 20,000 lb. per sq. in. between the different spring washers, maximum 1,810 inch-pounds, minimum 1,400 inch-pounds, as contrasted with the much smaller differences (1,580 to 1,670) found for the regular nuts is probably due to two causes; differences in the coefficient of friction and differences in the effective bearing radius of the washer on the nut. The two largest values are 1,810 inch-pounds for device FF, which has knurled bearing faces, and 1,800 inch-pounds for device CC, which has the largest outside radius of any of the spring washers.

Except for devices EE, FF, and GG, the difference between screwing-on and initial screwing-off torque at 20,000 lb. per sq. in., is considerably greater than the theoretical difference $0.0141\ S = 282$ inch-pounds, the maximum being 470 inch-pounds for device II.

This is in marked contrast to the smaller values found for the regular nuts.

The only reasonable explanation seems to be a change in the effective bearing radius of the washer between screwing-on and screwing-off. A decrease of 0.2 in. would account for the discrepancy for II. The faces of the bearing washers (EE and FF, fig. 75, and JJ, fig. 76) show after test that the radius of the scores made in screwing off were in several cases at least 0.2 inch less than those made in screwing on.

As can be seen from Figures 74 to 76, all of the spring washers scored the bearing surface of the nut and the bearing washer.

In continuous screwing off the unscrewing stress at first decreased until the nut was sufficiently loosened to allow the edge of the spring washer to cut into the face of the nut and the bearing washer. The device II was the only exception to this. Its edges cut into the nut immediately, when the nut was unscrewed, so that the continuous unscrewing torque increased slightly over the initial value before decreasing. The cutting of the nut and the bearing washer increased the frictional resistance, causing the screwing-off torques in all cases finally to exceed the screwing-on torques for the same stress. In many cases the torque actually increased at times and then decreased suddenly, sometimes two or three times in succession. These irregularities were probably caused by breaking of the chip in the face of the nut. As the size of the chip increased, the torque increased. When the chip broke the torque decreased suddenly.

In Figures 77, 78, and 79 and in Table 6, from which they are plotted, it must be remembered that for devices *I*, *II*, and *III* (regular nuts) in which the individual specimens gave more uniform results than

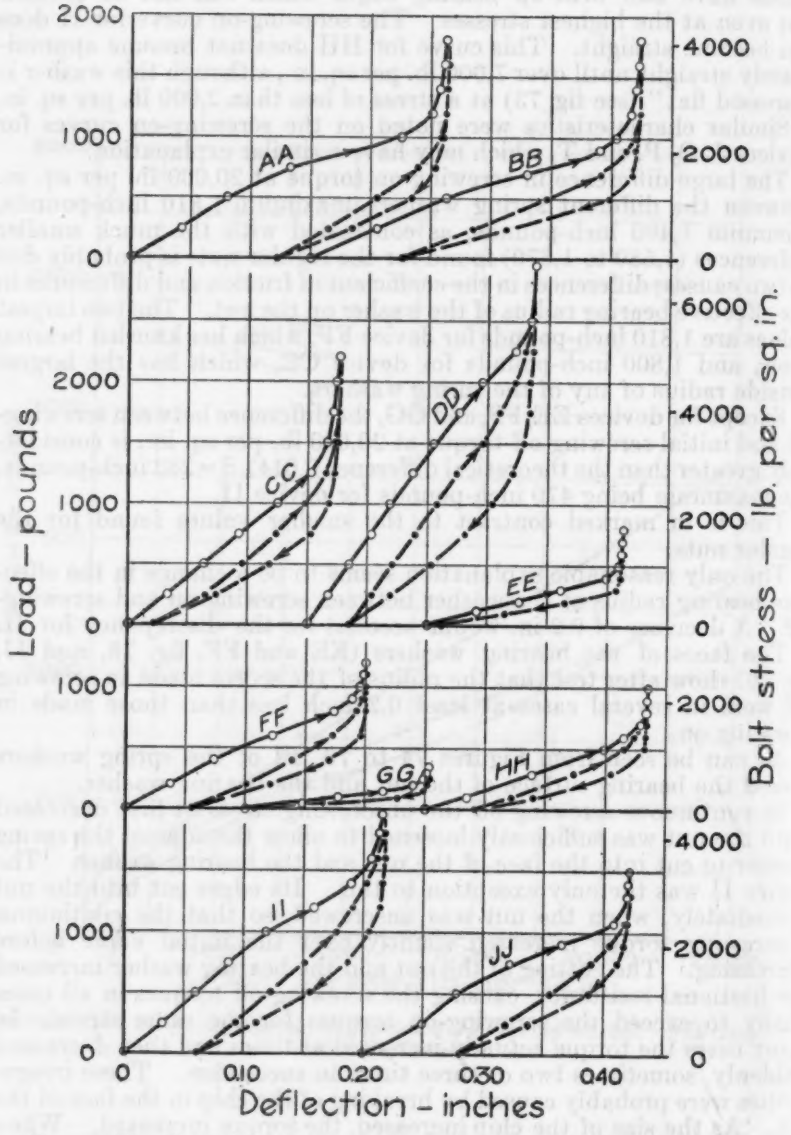

FIGURE 73.—*Load-deflection curves for devices AA to JJ, spring washers*

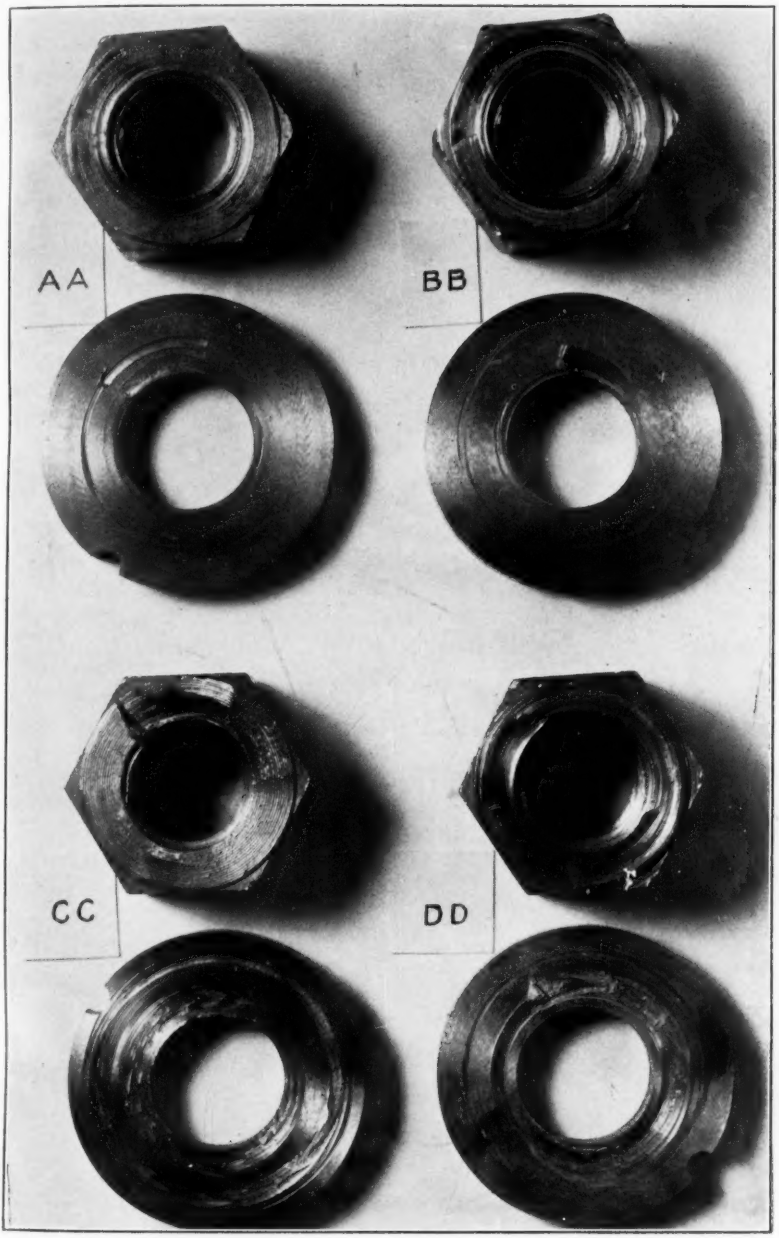

FIGURE 74.—*Bearing washers and regular nuts after test for devices AA to DD spring washers*

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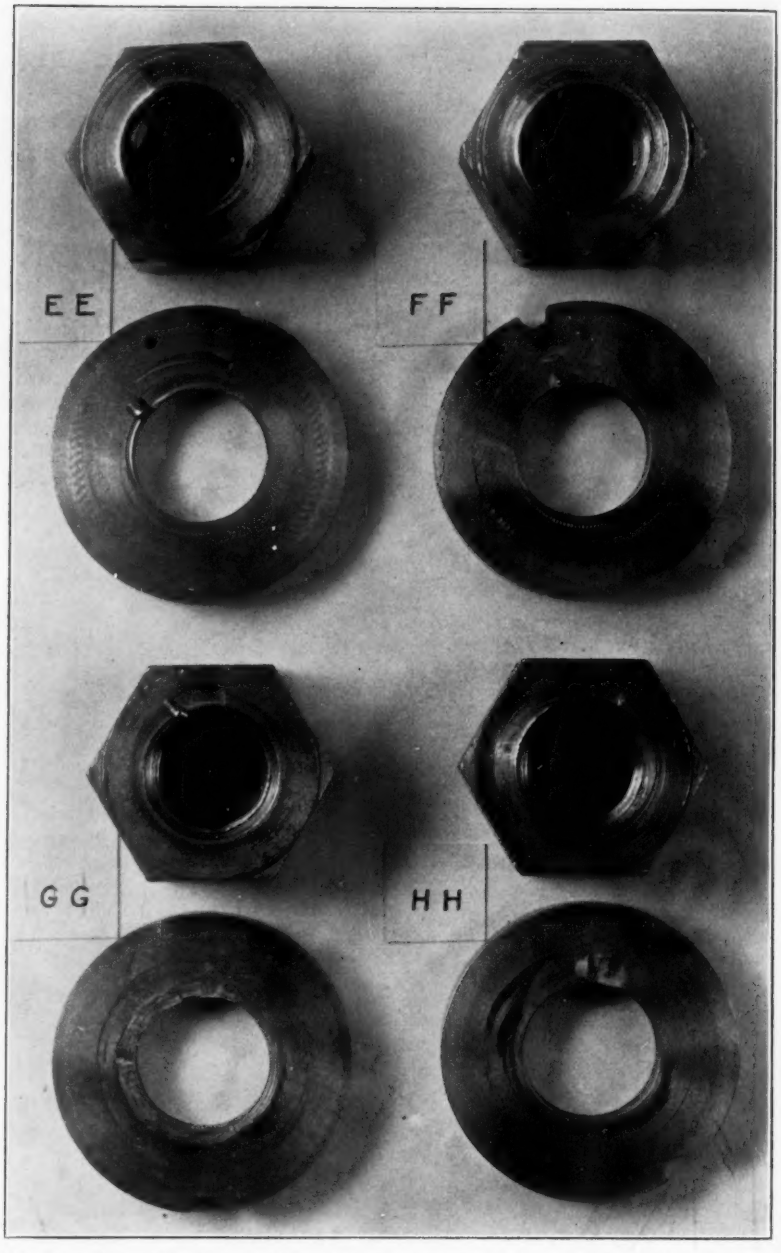

FIGURE 75.—*Bearing washers and regular nuts after test for devices EE to HH spring washers*

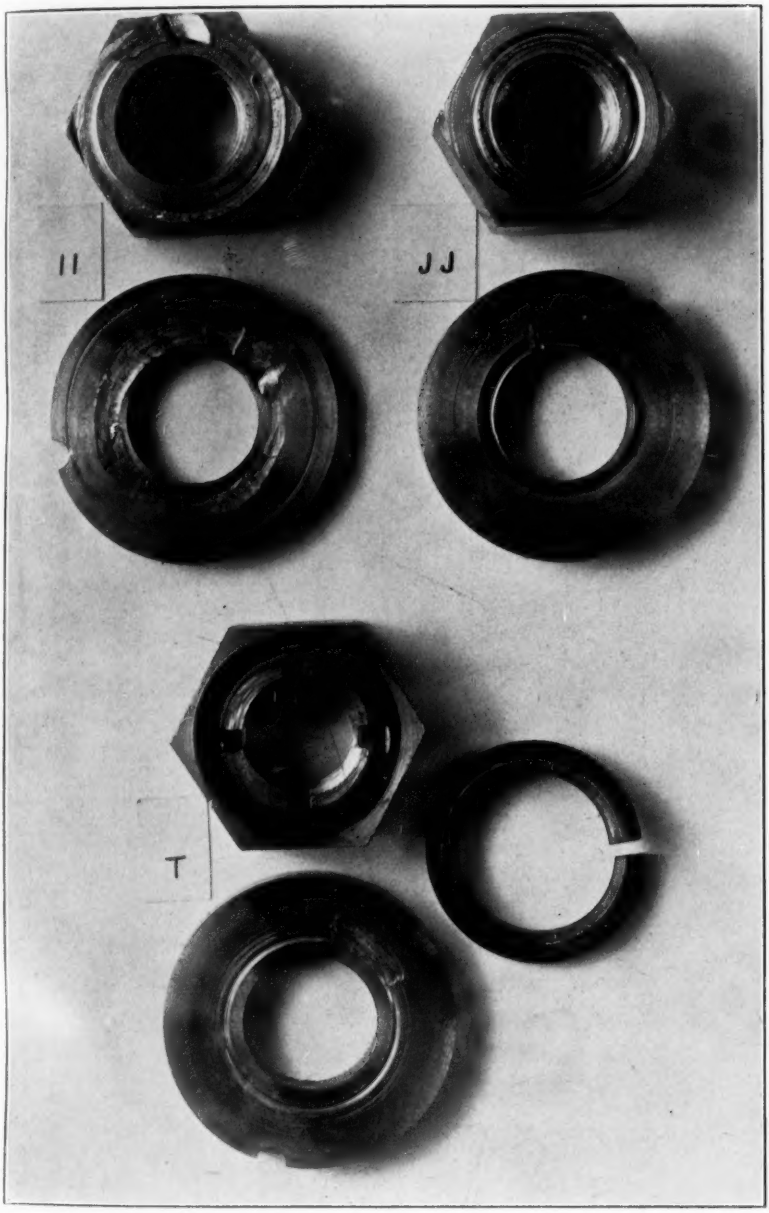

FIGURE 76.—*Bearing washers and regular nuts after test for devices II and JJ spring washers; also bearing washer and nut for device T*

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for practically all the other devices, differences of over 6 per cent in torques were found between individual specimens and the mean of a group, and also between groups of nominally identical specimens under identical test conditions. Conclusions based upon differences of plus or minus 6 per cent or less are therefore not warranted. A retest of any one of the devices might place it in order above or below all of the devices whose initial unlocking torque did not differ from its value by more than 6 per cent in the present series of tests, at the stresses chosen for comparison. In addition, in many cases the initial screwing-off torques at 10,000 lb. per sq. in. are read from extrapolated curves. It is doubtful whether or not these values can be relied upon to within 10 per cent.

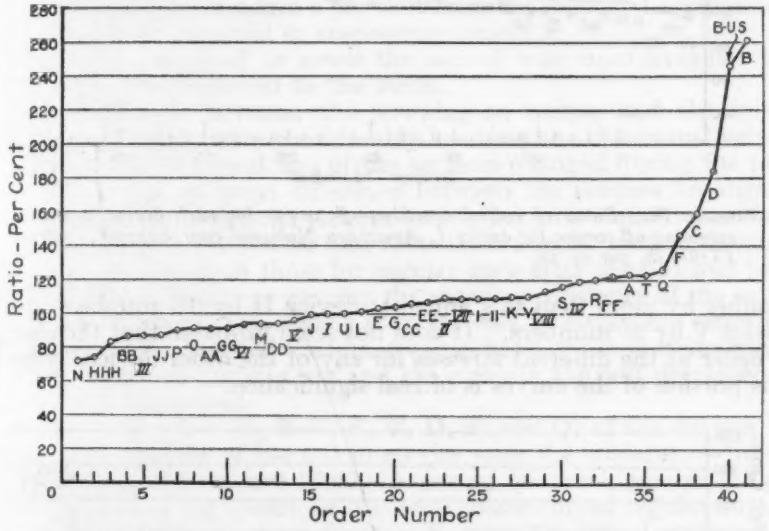

FIGURE 77.—*Ratio of initial screwing-off torque for each device to initial screwing-off torque for device I, American National coarse thread. Stress 10,000 lb. per sq. in.*

The curves of Figures 77, 78, and 79, may each be divided into two portions, the first portion containing the first 35 specimens in order and the second the last six specimens, B, B–U. S., C, D, F, and Q. The first portion in each case slopes upward, roughly following a straight line; for Figure 77, approximately 6 per cent for every five numbers; and for Figures 78 and 79, approximately 6 per cent for every seven numbers. A change of plus or minus 6 per cent in initial screwing-off torque for any device might shift it over a range of 10 to 14 numbers on this portion of the curves. That these ranges are rather too small than too large is shown by a comparison of the order numbers of devices *IV* and *V* at the three different stresses. These are both regular nuts with jam nuts, differing only in that one nut is slightly larger across the flats. Device *IV* shifts from order number 31 to 19, a decrease of 12 numbers, as the stress increases from 10,000 to 20,000 lb. per sq. in., while device *V* shifts

in order number from 14 to 29, an increase of 15 numbers. Comparison of the order numbers of the different devices at the three different stresses shows that only two devices change their order

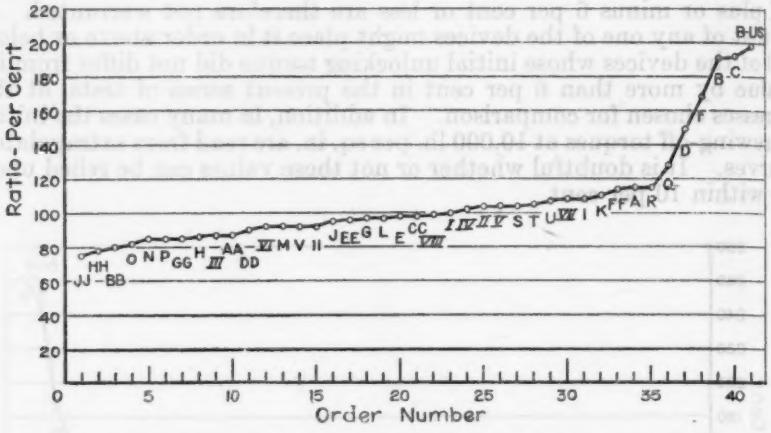

FIGURE 78.—*Ratio of initial screwing-off torque for each device to initial screwing-off torque for device I, American National coarse thread. Stress 15,000 lb. per sq. in.*

number by more than this amount; device II by 16 numbers and a device V by 20 numbers. It does not seem probable that the change of order at the different stresses for any of the other devices lying in this portion of the curves is of real significance.

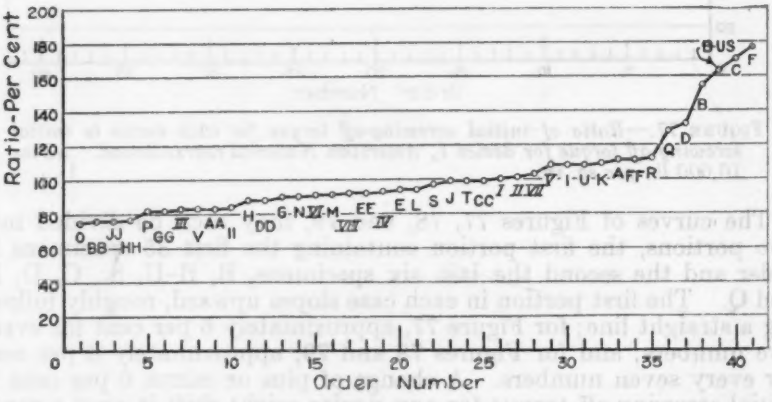

FIGURE 79.—*Ratio of initial screwing-off torque for each device to initial screwing-off torque for device I, American National coarse thread. Stress 20,000 lb. per sq. in.*

The five devices in the second portion of the curve show at all these stresses initial screwing-off torques over 25 per cent greater than the device *I*, American National coarse-thread regular nut.

X. CONCLUSIONS

Tests were made on 41 devices, including regular nuts (American National coarse thread, American National fine thread, and U. S. standard) and commercial devices for preventing rotation of the nut on the bolt in service to determine the relation between static tensile stress in the bolt (diameter ¾ in.) and the torque required to screw the nut on and to screw it off the bolt. The results lead to the following conclusions:

1. American National and U. S. standard nuts. The tests were in general agreement with Persy's theory. The torque required to screw on the nut was proportional to the stress in the bolt.

The torque required to screw on nominally identical nuts differed by more than plus or minus 6 per cent from the mean. Larger differences should be expected in engineering practice.

The torque required to screw the nut off was more irregular but still roughly proportional to the stress.

The differences between the screwing-on torque and the initial screwing-off torque were considerably less than the theoretical values, indicating that the condition of the surfaces changed during the test.

2. There was no great difference between the torques for regular nuts with jam nuts and the torques for regular nuts without jam nuts.

3. The torques for slotted and castellated regular nuts with cotter pins were greater than those for regular nuts after the nut had been screwed off sufficiently to develop the shearing resistance of the cotter pin. Unless the pin was a snug fit in the slot, however, the screwing-off torque never exceeded the initial value, because the shearing resistance of the cotter pin was low and the stress in the bolt decreased as the nut was unscrewed.

4. For only a few (B, B–U. S., C, D, F, and Q) of the devices for preventing rotation of the nut in service were the initial screwing-off torques for stresses above 10,000 lb. per sq. in. much greater (25 per cent) than those for American National coarse-thread regular nuts.

5. For only one of these devices, F, were the initial screwing-off torques higher than the screwing-on torques.

6. For all the other devices the ratio of the initial screwing-off torques to the initial screwing-off torques for American National coarse-thread regular nuts was distributed approximately uniformly between 72 per cent and 123 per cent at 10,000, between 75 per cent and 115 per cent at 15,000, and between 75 per cent and 112 per cent at 20,000 lb. per sq. in. stress in the bolt. The differences between individual specimens of any device were so large that it was possible to make only a rough arrangement of these devices in order, according to their initial unlocking torques.

Except for device V (and possibly II) there was no significant difference in their order of arrangement at the different stresses (10,000, 15,000, and 20,000 lb. per sq. in.).

7. When screwing off was continued, several of the devices, VII and VIII, slotted and castellated nuts with cotter pins, B, B–U. S., C, D, F, Q, T, and CC, EE, and II, spring washers, maintained, over a range of stress, torques relatively much higher than regular nuts.

8. When screwing off was continued to zero stress, over half of the devices required an appreciable torque to rotate the nut when the stress in the bolt was zero, and several devices, C, D, F, I, K, P, Q, S,

V, and AA and II (spring washers), consistently required a relatively higher torque to rotate the nut.

9. All of the spring or lock washers roughened the bearing surface and the face of the nut. After closing flat they were all permanently deformed. As the nut was screwed off, the torques were at first about the same as those for regular nuts. When the nut had rotated sufficiently for the ends of the washer to cut into the surfaces and offer considerable resistance to rotation, the stress in the bolt had, for many of the spring washers, been reduced to a low value.

WASHINGTON, September 30, 1931.

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